Evaluation of the Phase IIa Pilot-scale Limited Engineering Design Study Testing of the Zimpro Wet Air Oxidation Process to Treat NSCMP H Neutralent Simulant

Prepared for:

Non-Stockpile Chemical Materiel
Program Manager

Contract No.: DAAM-01-96-D-0010

Stone & Webster, Inc.
A Shaw Group Company

February 2002

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United States Army

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Chemical Demilitarization Project

Report No. R37V-10

Revision 0

February 2002

Approved By: ______________________

Stone & Webster Project Manager

Government Release By: ______________________

NSCMP Task Manager

EXECUTIVE SUMMARY

This report evaluates the results of the Phase IIa Pilot-scale Testing conducted for the Non-Stockpile Chemical Materiel Program (NSCMP) of the Wet Air Oxidation (WAO) process developed by USFilter/Zimpro (Zimpro) of Rothschild, Wisconsin. Stone & Webster, Inc. (Stone & Webster) managed these limited engineering design study tests on behalf of NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) to evaluate the process' applicability to the treatment of NSCMP feeds – specifically H neutralent simulant. The WAO process is commercially mature and all testing was conducted in an established pilot plant. The testing at Zimpro occurred over the period of November 12 – 16, 2001.

WAO is a liquid phase reaction in water using dissolved oxygen to oxidize wastewater contaminants. The oxidation reactions occur at moderate temperatures of 300^{o}F to 660^{o}F (150 – 350^{o}C) and at pressures from 150 to 3000 pounds-per-square-inch (psi). The process can convert organic contaminants to carbon dioxide, water and biodegradable short chain organic acids. The Zimpro design is a tower reactor with the preheated feed and oxidant introduced in the bottom. The oxidation process is exothermic and the generated heat is absorbed by the water and recovered by preheating the feed. Typically WAO processes are operated at temperatures of 270 to 300^{o}C and 2 to 6 percent organic material in the feed. After processing in the reactor, the effluent is cooled, depressurized and sampled to ensure the efficacy of the treatment. A portion of the WAO process effluent was collected and subjected to post treatment using a UV/O_3 process.

Testing in the bench-scale apparatus demonstrated the efficacy of the WAO process on NSCMP feeds. The principal objective of this phase of the testing was to assess the performance of the continuous-flow WAO process as applied to processing a feed simulating H neutralent simulant. The process was evaluated based on two main test objectives:

1) Demonstrate WAO efficacy in treating the selected liquid feeds at the Maximum Continuous Flow (MCF) rate of the existing pilot unit.
2) Demonstrate steady-state continuous, safe operation of the WAO system in a configuration similar to that of a full-scale system.

Test data and observations from the test runs were evaluated in accordance with the test criteria as described in Section 1. Test conclusions based on these criteria are summarized below.

Test data and observations were evaluated in accordance with the test criteria as described in Section 1. Test conclusions based on these criteria are summarized below.

- The Zimpro WAO process operated continuously for an 8-hour performance test at the pilot unit's maximum flow rate of 7.0 gallons-per-hour of total feed which corresponded to 0.23 gallons-per-hour of H neutralent simulant.
- Operating at a temperature of 300^{o}C with a 60 minute residence time, the WAO process demonstrated:
    - A TOC destruction efficiency of 97.57 for H neutralent simulant producing a liquid effluent with a TOC of less than 300 ppm.

  - Carbon-sulfur bond destruction efficiencies in excess of 99.9999%.
- The WAO reactor inlet experienced blockage during work-up testing (believed due to salt precipitation) which was eliminated by instituting an hourly 5-minute water rinse. The rinse was incorporated in the performance test operating protocol and was successful. This operating philosophy should be acceptable and successful in a full-scale design.
- Post-treatment of the WAO residual using UV/Ozone oxidation could not be adequately evaluated. The WAO liquid residual contained such low levels of contaminants that the performance of the post-treatment could not be quantified.
- The liquid residuals from the process contained various concentrations of metals attributed to corrosion of the reactor vessel. Materials of construction and corrosion management need to be addressed through additional studies in subsequent phases.
- The liquid effluent from the WAO test contained trace amounts of several volatile organic compounds, but none were at a level that would pose a problem with final disposal of the liquid effluent.
- Based on the test results, Zimpro developed a preliminary full-sized processing concept. The fixed unit would process up to 10 gallons-per-minute of dilute NSCMP materiel (H and GB neutralents and DF and QL binary products). Zimpro estimated an order-of-magnitude capital cost for the WAO-only system as $ 4,500,000. Additional equipment (UV/O_3 and Fluoride/Phosphorus precipitation) may be necessary to further treat the WAO effluent before disposal, increasing the total system cost.

Based on these conclusions, it is recommended that:

- The WAO full-sized processing concept should be compared to the other candidate low to moderate temperature and pressure processes (chemical oxidation and UV oxidation). If justified by the analysis, WAO testing should proceed as follows:
  - Pilot testing of all simulants should be conducted to identify the potential for plugging on the reactor system with the alternate feedstocks and evaluate operational alternatives to control or eliminate this phenomenon.
  - A material of construction and corrosion management testing program should be initiated to identify appropriate materials of construction and provide a quantitative indication of the reliability of the materials for pilot and full-scale operation. The MOC test program should include:
    - Testing of all prospective feed materiel (H and GB neutralents and DF and QL).
    - Appropriate long duration exposure of materials to WAO conditions.
    - Evaluation of achieving corrosion management through chemistry control.
    - A rigorous materials testing protocol including pre-inspection of the test coupons.
  - A series of tests should be initiated through ECBC to evaluate biotreatment of the WAO process effluent

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ACRONYMS & ABBREVIATIONS	**DEFINITIONS**
ACWAP	Assembled Chemical Weapons Assessment Program
APG	Aberdeen Proving Ground
ATAP	Alternative Technologies and Approaches Program
ASME	American Society of Mechanical Engineers
ASTM	American Society of Testing & Materials
CDP	Chemical Demilitarization Program
COD	Chemical Oxygen Demand
CWC	Chemical Warfare Convention
CWM	Chemical Warfare Materiel
DBA	Dibutyl amine
DCE	1,2-dichloroethane
DF	Methylphosphonyldifluoride
DMMP	Dimethyl methylphosphonate
DMSO	Dimethyl sulfoxide
ECBC	Edgewood Chemical and Biological Command
EDS	Explosive Destruction System
EMPA	Ethylmethylphosphonic acid
EPA	Environmental Protection Agency
FOTW	Federally Operated Treatment Works
GB	Chemical agent, Nerve agent, Sarin
GC	Gas Chromatography
H	Chemical agent, Mustard
MEA	Monoethanolamine
MDL	Method Detection Limit
MOC	Materials of Construction
MMD	Munitions Management Device
MPA	Methyl Phosphonic Acid
MPY	Mils-per-year
MS	Mass Spectroscopy
MSA	Methyl Sulfonic Acid
NMR	Nuclear Magnetic Resonance
NO_x	Nitrogen Oxides
NSCM	Non-Stockpile Chemical Materiel
NSCMP	Non-Stockpile Chemical Materiel Program
ORP	Overarching Research Plan
PACT	Powdered Activated Carbon Treatment
PBNSF	Pine Bluff Non-Stockpile Facility
PDHID	Pulsed Discharge Helium Ionization Detector
PMCD	Program Manager for Chemical Demilitarization
ppb	Parts per billion

ACRONYMS & ABBREVIATIONS	**DEFINITIONS**
ppm	Parts per million
psi	Pound per Square Inch
QL	O-(2-diisopropylaminoethyl) O'-ethyl methylphosphonite
RCRA	Resource Conservation and Recovery Act
RCWM	Recovered Chemical Warfare Materiel
RRS	Rapid Response System
SwRI	Southwest Research Institute
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
UV	Ultraviolet
WAO	Wet Air Oxidation
Wt	Weight
Zimpro	USFilter/Zimpro Products

Evaluation of the Phase IIa Pilot-scale
Limited Engineering Design Study Testing
of the
Zimpro Wet Air Oxidation Process to Treat
NSCMP H Neutralent Simulant

1. Introduction

This report evaluates the results of the Phase IIa continuous pilot-scale testing of the Wet Air Oxidation (WAO) process developed by USFilter/Zimpro (Zimpro) of Rothschild, Wisconsin. Stone & Webster, Inc. (Stone & Webster) managed these tests to evaluate the process' applicability to the treatment of Non-Stockpile Chemical Materiel Program (NSCMP) feeds. This testing is a follow-up to earlier batch testing at the bench-scale, which demonstrated the efficacy of the WAO process[1]. The principal objectives of this phase of the testing were to assess the performance of the continuous-flow WAO process as applied to processing a feed simulating H neutralent.

Zimpro conducted these tests using their existing equipment and procedures in their established pilot plant facility under a subcontract to Stone & Webster on behalf of the NSCMP. Stone & Webster also subcontracted ENSR and Southwest Research Institute (SwRI) for analytical services in support of the performance test.

This section discusses the objectives of the Pilot-scale Tests and the Evaluation Criteria that Stone & Webster developed to assess the WAO process performance. Section 2 of this report provides background information on the technology as well as the rationale for selecting WAO for testing. Section 3 describes the physical equipment that was tested. Section 4 describes the testing approach and procedures for the test runs completed. The results of the tests are presented in Sections 5, 6 and 7. Section 5 is a discussion of the WAO testing. Section 6 presents the testing of post-treatment of the WAO effluent. Section 7 reports the results of the combined WAO and post treatment processes. Section 8 contains a discussion of the WAO process' applicability to the NSCMP, including a processing concept for full-scale application. Sections 9 and 10 include the test conclusions and recommendations for further action, respectively.

1.1 Objectives

The objective of Phase IIa was to perform limited engineering design study testing to evaluate the Zimpro Wet Air Oxidation treatment process for treating H-neutralent. Previous batch studies at the bench-scale indicated that the WAO process could effectively destroy the relevant compounds in a simulated neutralent mixture. This testing was initiated to evaluate the WAO process operating on a continuous basis at the pilot-scale. To support evaluation of this objective, Stone & Webster developed a series of evaluation criteria that would allow determination as to whether the specific test objectives have been met. These test objectives were the basis for the formulation of the test plan and included:

1) Demonstrate WAO efficacy in treating the selected liquid feeds at the Maximum Continuous Flow (MCF) rate of the existing pilot unit.

2) Demonstrate steady-state continuous, safe operation of the WAO system in a configuration similar to that of a full-scale system.

1.1.1 Demonstrate WAO efficacy at MCF

While the effectiveness of WAO as a treatment for simulated neutralent was demonstrated in batch studies at the bench-scale in a previous study, the process performance in a continuous flow system has not been demonstrated or quantified. WAO is commercially applied as a continuous flow process, and the logical sequence in testing is to evaluate the process in a continuous pilot unit.

The Chemical Weapons Convention (CWC) requires that the chemical agents and their precursors be destroyed. While the facility permit determines the specific level of destruction, the materiel must have an overall destruction efficiency of at least 99.9 %. One of the key criterions that are being used to evaluate all processing systems for NSCMP applications is their destruction efficiency. It is necessary to determine the effectiveness of the continuous WAO process and determine if any post-treatment methods are necessary for WAO effluents.

Testing of the continuous flow pilot-plant at or near the maximum continuous flow (MCF) is conducted to identify any processing limitations that may occur in a commercial system. The philosophy is that a full-scale unit would be designed based on a flow rate that correlated to the required throughput. The testing was designed to operate the pilot unit at conditions that would be prototypical of full-scale to ensure that operating parameters (flow rates and velocities) within the unit operations reflected normal operation. In this manner, any physical or chemical limitations of the process could be identified.

1.1.2 Demonstrate Steady-state Operation of WAO System Similar to Full-scale Configuration

A goal of the limited design study testing is to develop sufficient operating data to support the development of a full-scale design concept. Prior to developing a design concept, it is necessary to verify the steady state, continuous, safe operation of the WAO system. The WAO system tested must be prototypical of a full-scale system to demonstrate the efficacy of the process to support design development, or identify data gaps that need to be filled through further testing.

1.2 Evaluation Criteria

Associated with the test objectives are specific criteria that were used to evaluate the effectiveness of the testing. The evaluation criteria and associated objectives are discussed below.

1.2.1 Demonstrate WAO efficacy at MCF

The effectiveness of the continuous WAO process to adequately treat the H-neutralent simulant was evaluated based on the following criteria:

- All effluents/residuals demonstrate at least 99.9% destruction efficiency of simulant compounds or relevant byproducts/bonds based on WAO feed
- Automatic operation at MCF with all systems controlled and no system function overridden for the duration of the tests
- Characterize solid, liquid, and gaseous effluents

1.2.2 Demonstrate Steady-state Operation of WAO System Similar to Full-scale Configuration

The steady-state operation of the WAO process in a configuration similar to a full-scale system was evaluated based on the following criteria:

- Pilot-scale system operates for a minimum of 8-hours at steady-state and MCF
- WAO system demonstrates operations that are prototypical of a full-scale system including:
  - Handling of simulated materials
  - Process control and data acquisition
  - Configuration and type of equipment
  - Unit operations in the system

2. Background

2.1 Technology Evaluation and Development for NSCMP

The U.S. Army Program Manager for Chemical Demilitarization (PMCD) established the NSCMP with the mission to provide centralized management and direction to the Department of Defense for the disposal of non-stockpile chemical materiel in a safe, environmentally sound and cost effective manner. The NSCMP includes five categories of chemical warfare materiel (CWM): binary chemical weapons; former production facilities; miscellaneous CWM; recovered chemical weapons; and buried CWM. Substantial differences exist between CWM in the Stockpile and Non-Stockpile programs. Whereas the stockpiled CWM is present in larger quantities, non-stockpile CWM encompasses a greater variety of materiel with far more physical configurations and agent-fill types. The variety, locations and deteriorated physical condition of non-stockpile CWM pose unique requirements for treatment systems.

To support accomplishment of its mission, the NSCMP developed an Overarching Research Plan[2] (ORP) which establishes the goals, requirements, and approaches for evaluating and developing technologies for the safe and efficient disposal of non-stockpile CWM. The ORP identifies systems that NSCMP has and is continuing to develop to meet its mission goals. The ORP also identifies additional needs and associated schedule to support accomplishment of these goals. The ORP identified Near-Term, Intermediate-Term and Long-Term applications for technologies to treat the broad range of NSCMP wastes.

WAO has been previously evaluated for applicability in the Chem-Demil Program. An evaluation of alternatives to incineration conducted in 1993[3] discussed the WAO process and noted its commercial maturity and potential applicability. Specifically noted was the significant operating history and the operating advantage of the moderate temperature aqueous processing environment producing a gaseous effluent free of SO_2, dioxins, particulate matter, and NO_x. The evaluation also discussed the relevancy of previous pesticide testing of materials with similar bond structures to CWM, where specific compound destruction efficiencies in excess of 99% were observed. It should be noted that the destruction efficiencies were based on analyses of the specific compound of interest, and did not evaluate or consider the reaction byproducts. For example, while WAO effectively destroyed DMMP in previous tests, the major byproduct was methyl phosphonic acid, which is a Schedule 2B compound that is controlled under the CWC.

In 2001, the National Research Council published an evaluation of alternative processing technologies for the disposal of neutralent wastes[4]. The study focused on non-incineration, alternative technologies for the treatment of liquid neutralents from the Rapid Response System (RRS) and Munitions Management Device (MMD). Eight technologies were evaluated and ranked based on a variety of criteria. Wet air oxidation was ranked second out of the eight in potential to effectively treat the RRS and MMD neutralents. It should be noted that the evaluation committee acknowledged a bias towards technologies that operated at low temperatures and pressures.

NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) charged Stone & Webster with conducting an evaluation of the Zimpro WAO process. The evaluation was completed in April 2001 and recommended that testing of WAO be conducted at the bench-scale to determine its applicability for NSCMP feedstocks. In addition, limited continuous flow testing was to be conducted at the pilot-scale to evaluate to performance of the process[5]. These initial engineering design studies would be used to develop a processing concept for the NSCMP application at Pine Bluff Arsenal as a basis.

In August 2001, Stone & Webster initiated a test program with Zimpro to test the WAO process at the bench-scale on simulated NSCMP neutralents and binary products. Targeted materiel for this testing included surrogates of chemical agent neutralents, GB and H, as well as binary products, DF and QL. The preliminary bench-scale batch testing was used to establish the operating conditions of temperature and residence time (initially 320 ^oC and 60 minutes) for the H neutralent simulant pilot testing. At the designated operating conditions, bench-scale destruction efficiencies of greater than 99.99% of the surrogate compounds (dimethyl methylsulfoxide and dichloroethane) was achieved.

2.2 Wet Air Oxidation

Wet Air Oxidation (WAO) is a liquid phase reaction in water using dissolved oxygen to oxidize organic wastewater contaminants. The oxidation reactions occur at moderate temperatures of 300°F to 660°F (150° - 350°C) and at pressures from 150 to 5000 pound per square inch (psi). The process can convert organic contaminants to carbon dioxide, water and biodegradable short chain organic acids. Inorganic constituents such as sulfides and cyanides can also be oxidized.

In the WAO reaction, complex organic molecules are broken into simpler organic compounds or to a complete mineralized state (CO_2, NH_3, Cl^-, $SO_4^=$, PO_4^{-3}). In practice, the complex organic feeds are generally not completely mineralized. Simple organic compounds such as low molecular weight carboxylic acids and mineralized reaction products will be present in the process effluents. Because of the presence of the low molecular weight carboxylic acids, the WAO effluent generally requires further treatment. Standard treatment techniques include activated sludge biotreatment or UV oxidation. Post treatment of the WAO effluent from the oxidation of the neutralized chemical warfare materiel is anticipated.

WAO is an established technology with over 50 years of commercial history in a variety of industrial applications. Originally developed in the 1930’s as a process to produce artificial vanilla (vanillin) from pulping liquor by partial oxidation of the ligno-sulfonic acids, it was patented as a waste treatment process in 1950. The waste treatment technology was introduced to the pulp and paper industry in 1955 and to the municipal sewage sludge market in the early 1960’s to treat biosolids from the activated sludge process.

The Zimpro WAO process is in operation worldwide treating a variety of complex waste streams including sludges from municipal and industrial wastewater treatment, pulp and paper wastes, and spent caustics from ethylene process facilities, oil refineries and other industries. The process has a long history of successful full-scale operation with more than 150 commercial applications as follows:

- 85 Low-pressure oxidation systems for sludge dewatering.
- 14 Intermediate-pressure oxidation systems for autothermal sludge destruction/dewatering.
- 7 High-pressure oxidation systems for complete sludge destruction.

- 25 Wet air regeneration systems for powdered activated carbon regeneration and sludge destruction.
- 44 Industrial WAO systems for various applications.

Flowrates for commercial systems range from 2 to 300 gpm with designed temperatures ranging from 150 - 320ºC (300 - 610°F) and 100 – 3800 psia utilizing either air or pure oxygen as the oxidant source.

The WAO process is fabricated from readily available commercial equipment. Typical materials include titanium, stainless steels and specialty alloys (Inconel™ and Hastelloy™). The use of "exotic" or "semi-precious" materials is generally not required.

2.3 Post-Treatment

It was anticipated that the effluent from WAO treatment of the NSCMP feedstocks would contain short-chain organic compounds, ammonia, and may contain trace levels of Schedule 2 compounds. Thus, the WAO effluent is expected to require further processing to meet the overall treatment objectives of greater than 99.9% destruction of the CWC schedule compounds and an overall TOC of less than 25 ppm. The post-treatment options that were considered by Zimpro for the WAO effluent were biotreatment, UV Oxidation (with H_2O_2 or O_3), or a combination of both.

After conducting preliminary post treatment process screening in the bench-scale testing, Zimpro recommended testing with UV oxidation with the addition of for the continuous pilot-scale tests effluent. The testing was to be conducted using a batch apparatus with the WAO treated H neutralent simulant.

2.4 Test Facility

The USFilter/Zimpro site located in Rothschild, Wisconsin is the largest WAO process research and development center in the world. Zimpro has been involved in evaluating WAO for a variety of feedstocks for 50 years. The test facility includes full bench-scale and pilot-scale testing capabilities. Zimpro's bench-scale laboratory includes more than 50 batch reactors (autoclaves) fabricated from a variety of alloys including, Nickel 200, Stainless Steel, Inconel™, Hastelloy™ and Titanium. Along with treatability studies, corrosion testing is also conducted on the bench-scale where the WAO reaction environment is simulated in the autoclave reactor.

Zimpro's pilot facility includes 4 independent and fully operational WAO units. The individual setups are flexible and include reactor trains constructed from different materials and various configurations. Zimpro has full manufacturing capabilities including ASME PP, R, and U Stamp certifications. Zimpro also holds a current RCRA Part-B permit at their pilot plant research facility applicable for pilot-scale testing and storage of hazardous waste.

In addition to the WAO facility, Zimpro is affiliated with Enviroscan; an in-house, full-service, EPA approved analytical laboratory that supports testing in the WAO research and development.

3. System Description

The Phase IIa testing of the WAO process to treat H-neutralent simulant was conducted by Zimpro at their facilities in Rothschild, Wisconsin. The testing included a continuous pilot-scale system and batch UV Oxidation apparatus that were developed and assembled by Zimpro. This section discusses the physical configuration of the test setups.

3.1 Pilot-scale WAO System

Zimpro used their S–2A Inconel™ 600 continuous flow WAO pilot unit for Phase IIa testing. The S-2A unit is capable of operating at flow rates from 1 to 7 gallons-per-hour of feed flow and temperatures up to 320 ^{o}C. All wetted parts of the S–2A pilot unit exposed to high temperature are constructed of Inconel™ 600. The process flow diagram of the pilot plant for this test is shown in Figure 3-1.

Prior to processing, the simulant feed was prepared, diluted and mixed in a stainless steel tank equipped with an agitator and recycle loop. Dilution of the feed material is required to limit the heat generated in the reactor. The WAO system is designed to process a feed material of approximately 70,000 ppm Chemical Oxygen Demand (COD). This corresponds to autothermal operation in which the feed generates sufficient heat during oxidation to maintain reactor temperature.

The mix tank recycle loop consisted of an air operated diaphragm pump and an in-line heat exchanger. The in-line plate heat exchanger removed any heat of reaction or dilution from the feed using tap water as the indirect cooling media. The cooling water flowed through the heat exchanger and into a break tank and overflowed to a drain. The pH of the break tank was measured to monitor for heat exchanger leakage.

The dilute feed was transferred from the mix tank to the WAO system feed tank. The stainless steel feed tank was equipped with an agitator, and capability to recycle the contents for additional mixing. A low-pressure centrifugal pump was used for both the recycle flow and to provide suction pressure for the WAO high-pressure feed pump.

A Mil Royal high-pressure diaphragm pump pressurized the feed stream to the full operating pressure of the reactor. Feed flow was set by manual adjustment of the pump stroke. The flow of the feed stream to the WAO pilot unit was monitored by the change of the liquid level in the feed tank as indicated by the site glass on the feed tank.

High-pressure air was mixed with the feed in line prior to the oil heater. The air was supplied by a four-stage air compressor and controlled by a manually operated needle valve. The operator set the airflow to the desired value as measured by an orifice/DP transmitter. The feed /air mixture then flowed to the inlet of the hot oil heater. The hot oil heater contained a 3/8-inch OD, 0.065-inch wall tube approximately 40 feet in length. The hot oil heater was thermostatically controlled by a temperature controller and heated the feed/air mixture to the required reactor inlet temperature. The hot feed /air mixture that exited from the hot oil heater fed directly to the bottom of the WAO reactor.

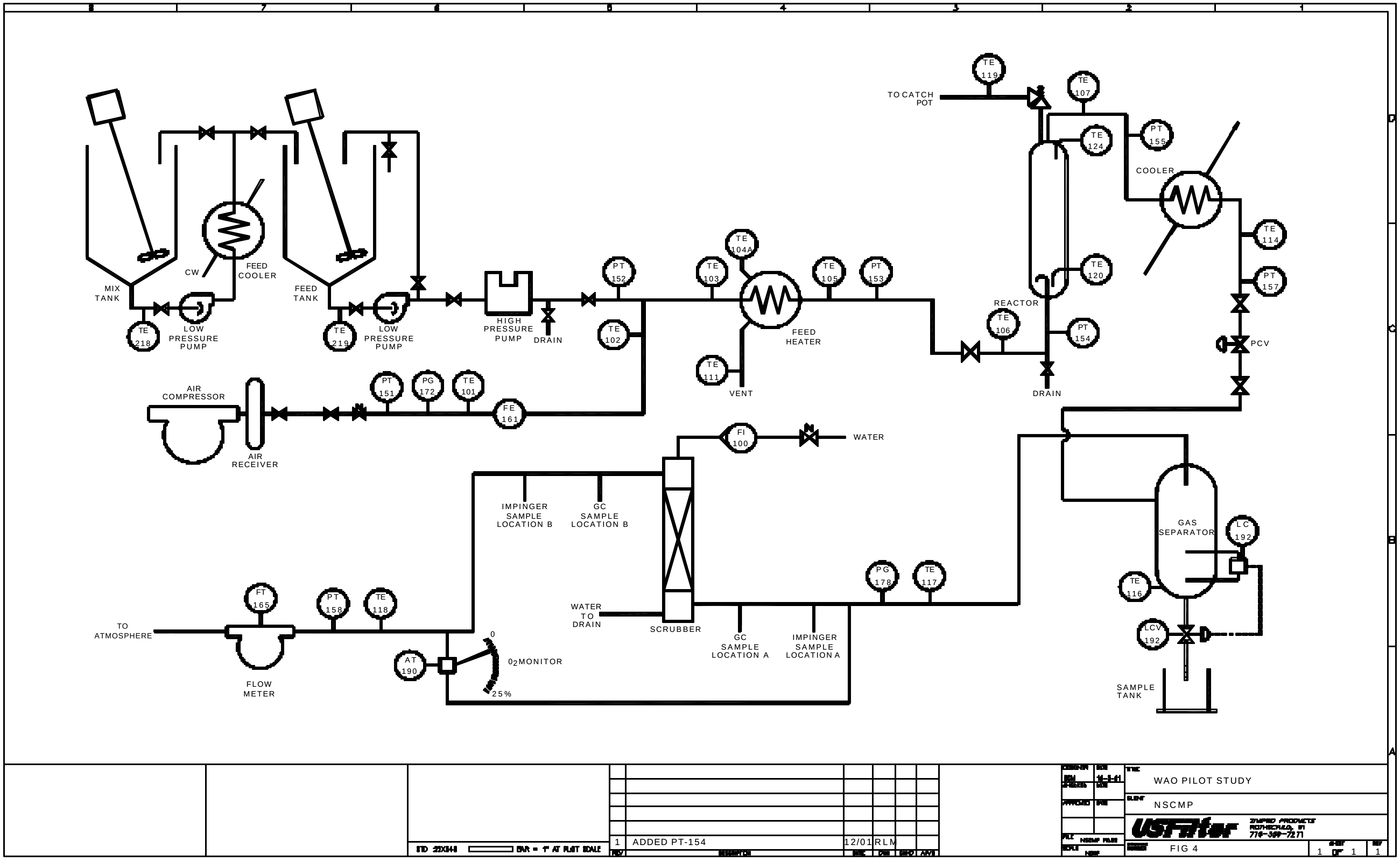

Figure 3-1 Process Flow Diagram

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

The WAO reactor was a 9.4-cm (3.7-inch) diameter by 3.8-m (12.5-foot) high baffled, bubble column. The total volume of the reactor was 6.9 gallons. Resistance temperature devices (RTD) were placed along the walls and in the top and bottom heads of the reactor to measure the reactor temperature.

The reactor effluent (oxidized liquid and offgas) exited the top of the reactor and proceeded to the tube side of two tube-in-tube coolers where it was cooled against water. The cooling water temperature was controlled to attain the desired oxidized liquid/offgas temperature. The effluent then passed through a pressure control valve (PCV), prior to an atmospheric low-pressure liquid/vapor separator. In the separator, the non-condensable offgas was separated from the oxidized liquid.

The non-condensable gas passed out of the separator and through a water scrubber. Downstream of the scrubber, a dry gas meter measured the gas flowrate. The offgas was then discharged through a vent stack outside the building with the aid of an induced draft fan. The scrubber system was bypassed during sampling periods of testing. An in-line oxygen analyzer prior to the scrubber continuously monitored the offgas. In addition, the offgas was analyzed for oxygen, carbon dioxide, nitrogen, carbon monoxide, total hydrocarbons (as ethane) and methane on an hourly basis by gas chromatography. Additional samples using impingers and grab techniques were obtained through preinstalled ports.

The oxidized liquid exited the separator through a level control valve. Level was maintained to ensure that no offgas could exit with the oxidized liquid. The liquid was collected in a container and flow rates determined recording the weight and specific gravity of the oxidized liquid collected every half-hour.

As shown in Figure 3-1, pressure transmitters, indicated by P, and temperature monitoring points (RTD's) indicated by TE, were located throughout the system for monitoring and control. Figure 3-2 is a photograph of the overall pilot plant and Figure 3-3 shows the tower WAO reactor.

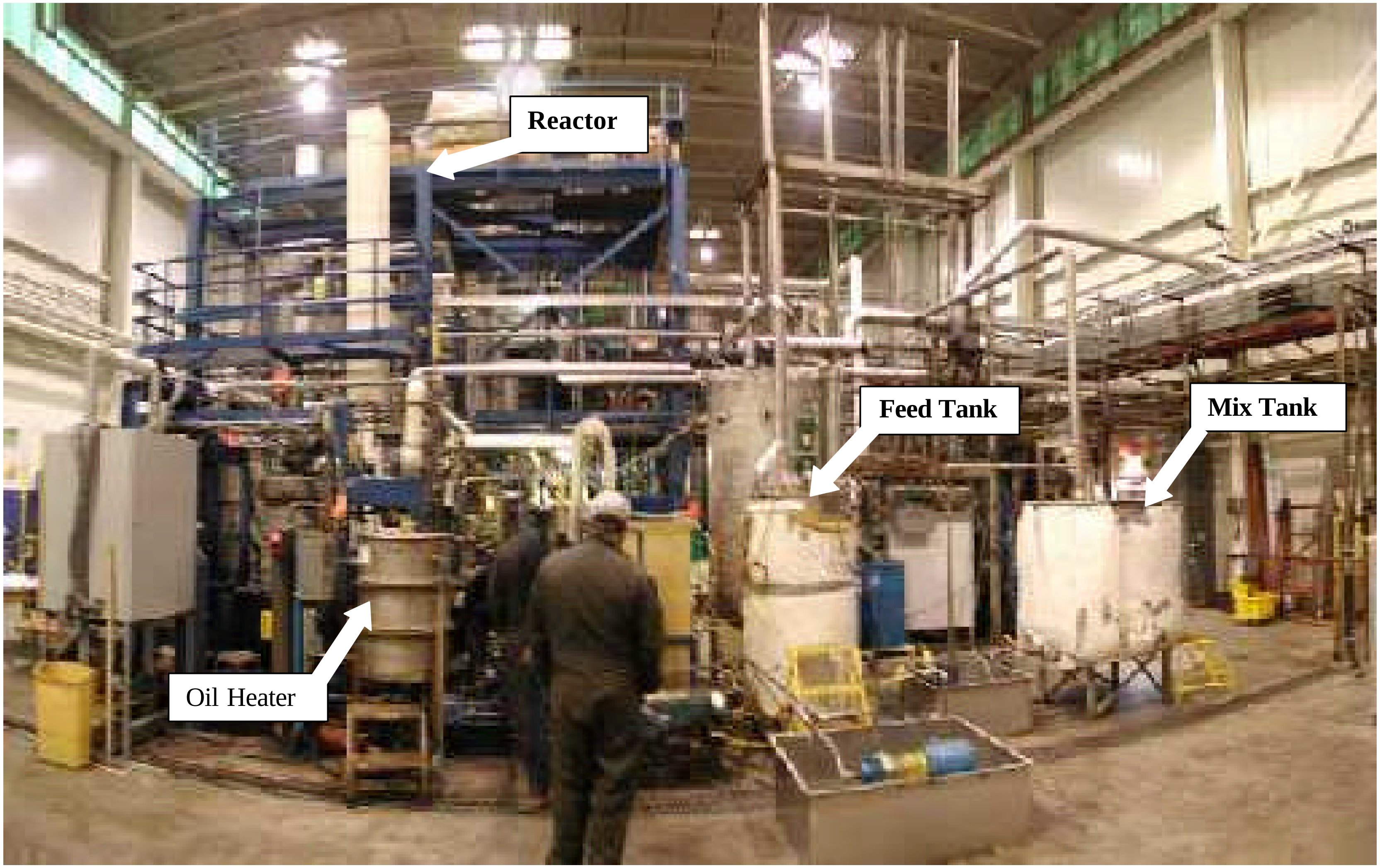

Figure 3-2 View of Overall Pilot Unit

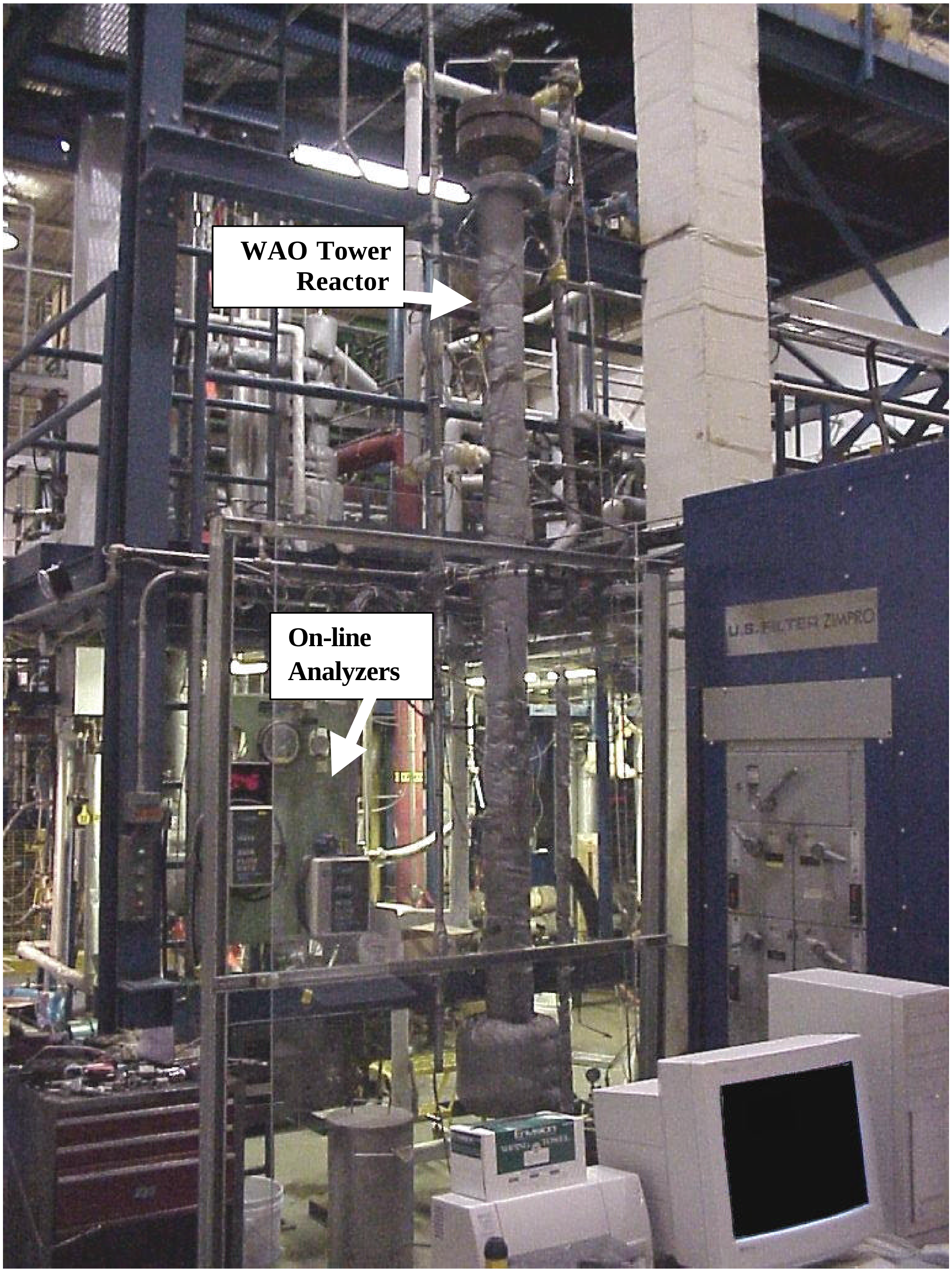

Figure 3-3 WAO Pilot Unit Reactor Vessel

3.2 Post Oxidation Test Equipment

Post oxidation treatment consisted of oxidation with ozone (O_3) enhanced by UV light. A batch bench scale system was used for this study. The WAO oxidized effluent contained a high concentration of dissolved carbonate, which was removed prior to treatment with ozone and ultra-violet light. The WAO effluent pH was adjusted with concentrated hydrochloric acid and placed in a gas sparging apparatus.

After the carbon dioxide was removed, the pH was adjusted back to approximately 10 with caustic and the material placed in the bench scale reactor. The reactor consisted of a 1.0 liter glass cylinder containing an ozone diffuser tube and an ultra-violet (UV) light. The UV light source was a medium pressure mercury vapor bulb (150 W) complete with power supply and ballast. Ozone was generated using a one pound per day Welsbach ozone generator.

Compressed air from a cylinder was used as the source of dry gas for the ozone generator. The contents of the bench scale reactor were thoroughly mixed by the action of the applied ozone containing gas and/or a magnetic stirrer. A schematic representation of the bench scale reactor is shown in Figure 3-4. A photograph is included in Figure 3-5.

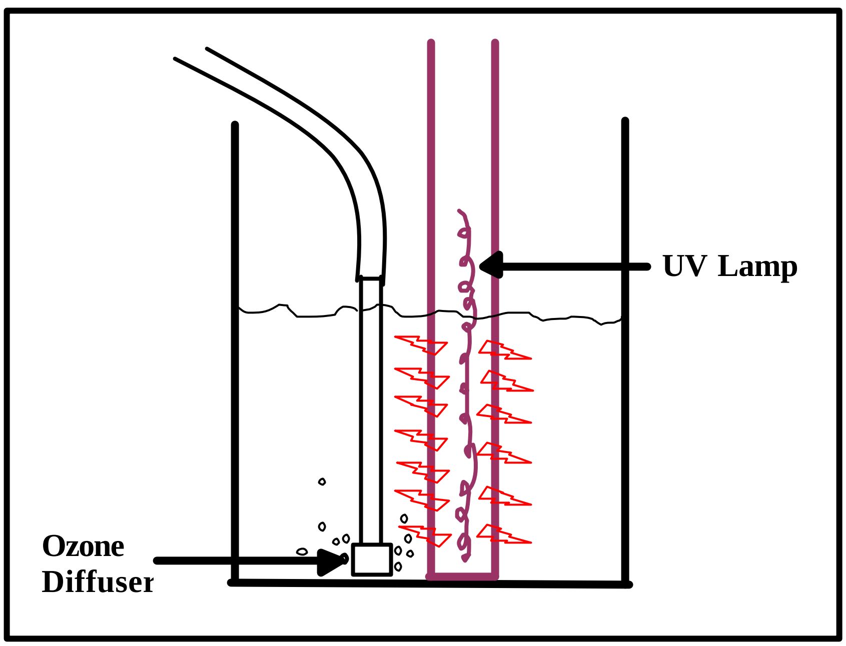

Figure 3-4 Schematic View of UV Oxidation Setup

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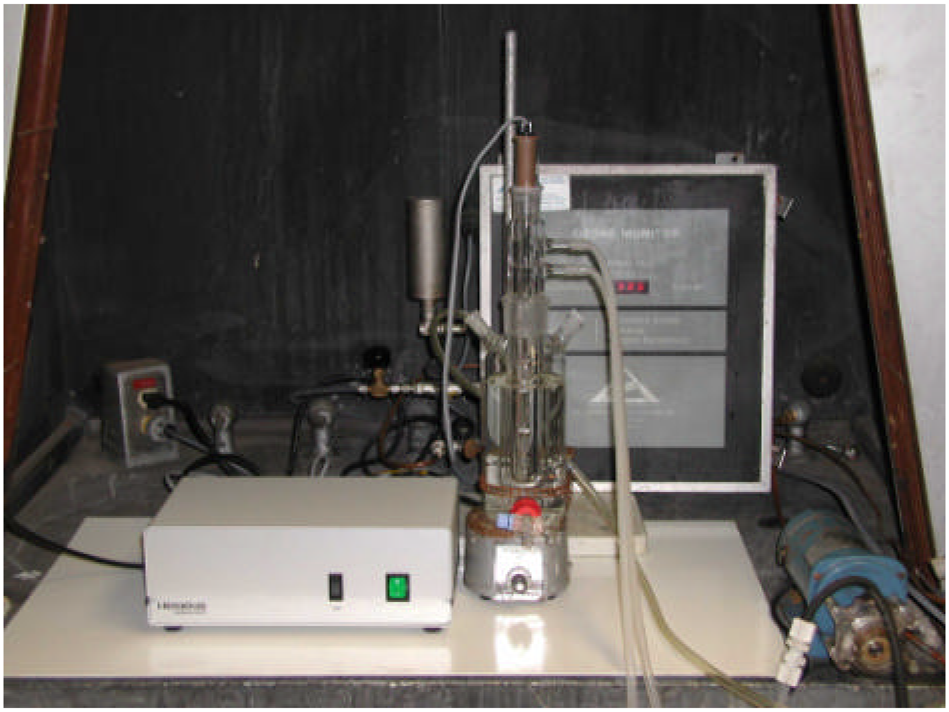

Figure 3-5 UV Advanced Oxidation Reactor with Medium-pressure UV Bulb

4. Test Description

This section contains a discussion of the work-up and performance testing that was conducted at Zimpro during the week of November 12, 2001. Included are the feeds tested, the tests performed, and the procedures that were used for the tests. The results of testing are discussed in Sections 5 and 6 for the WAO, and post treatment testing, respectively.

The Phase IIa WAO pilot study was completed in two parts - work-up and performance testing. Phase I of this overall test program, was a bench-scale study of WAO to determine the process operating parameters of temperature and residence time to achieve the required destruction. During Phase 1, Zimpro established the operating conditions at 320^{o}C with a residence time of 60 minutes[6]. This formed the starting point for the pilot testing.

The WAO pilot study consisted of five work-up runs, a performance test and a performance test extension. The purpose of the work-up runs was to verify the process operating conditions selected based on the bench-scale testing results, and develop the operational procedures used in a continuous flow WAO system for treating the H neutralent simulant. Following the work-up testing, an eight-hour performance test was conducted to validate the process and collect samples of process effluents and residuals for analysis. In addition, the WAO effluent was subjected to post-treatment testing using UV/O_3 oxidation in the same manner as the bench-test program, using the same apparatus. Stone & Webster witnessed the performance testing and an independent laboratory (ENSR) collected all residuals (gas and liquid) for analysis.

4.1 Feed Tested

All pilot testing was conducted on a simulant of the NSCMP MEA-based H neutralent. The simulant was developed to represent a mono-ethanolamine (MEA)-based Munitions Management Device (MMD) neutralent from the processing of a sulfur mustard (H) containing munitions. The simulant formulation was based on a 10:1 volume ratio of reagent to chemical agent.

The composition of the H neutralent simulant feed is shown in Table 4-1.

Table 4-1 H Neutralent Simulant Composition

Neutralent			Simulant		
Major Components	**Chemical Formula**	**Wt% in neutralent**	**Equivalent component in Simulant**	**Chemical Formula**	**Wt% in Simulant**
MEA	C_2H_7NO	78	MEA	C_2H_7NO	83.00
Water	H_2O	9.5	Water	H_2O	10.10
MEA HCL	$C_2H_8ON\ Cl$	7.25	Dichloroethane	$C_2H_4Cl_2$	3.90
HETM	$C_6H_{13}NOS$	5.25	Dimethyl sulfoxide	C_2H_6OS	3.00
TOTAL		**100**			**100.00**

4.2 Feed Analysis

Feeds were prepared in accordance with procedures that were developed by SwRI[7]. Zimpro prepared the feed with purchased stock chemicals. Three dilutions (20:1, 25:1 and 30:1) of the simulant in water (volume of simulant to volume of water) were tested in the work-up runs. The performance test used a 30:1 dilution of the H neutralent simulant in water. The mixing procedure Zimpro followed is included in Appendix C. During the performance test, two samples of the dilute WAO process feed were taken from the feed tank to coincide with the effluent sampling periods during hour 2 and 6 of the testing. Table 4-2summarizes the analyses of the diluted feed samples taken from the feed tank.

Table 4-2 Dilute Simulant Analysis

	H neutralent simulant		
Analyte	**Theoretical[1]**	**Sample (hr 2)**	**Sample (hr 6)**
Monoethanolamine, MEA (ppm)	26,774	34,000	40,000
Dichloroethane, DCE (ppb)	1,258,000	270	290
Dimethyl sulfoxide, DMSO (ppm)	968	545	530
TOC, (mg/L)	11,726	9,500	9,350
pH		13.46	13.51

1. Theoretical based on simulant preparation procedure

The analysis of the simulant samples varies significantly from the theoretical expectations. Discussions with the laboratory (SwRI) indicated that the high pH of the sample probably effected the accuracy of the analyses. For the purposes of calculating destruction efficiencies, a conservative approach was used whereas the theoretical analyses were used as the starting concentration, with appropriate dilution.

4.3 Test Procedure - WAO Testing

All testing (work-up and performance) was conducted in the Zimpro S-2A pilot plant described in Section 3.1. The unit is a permanent installation at Zimpro's Rothschild, Wisconsin pilot facility and all hot wetted parts are constructed of Inconel™ 600.

Prior to testing, the H neutralent simulant feed was prepared in the mixing tank. Initially water was used as a feed to start process flow. Once the system compressors and pumps were operating with water, airflow was introduced and the feed preheater and effluent cooling systems were started. As the unit was brought to operating conditions all data loggers, online analyzers, and control systems were started. Upon meeting the selected operating temperature at the reactor bottom with steady liquid and airflow rates, the unit was switched to the simulant feed. The specific sequence used by Zimpro to startup, operate and shutdown the system are included in Appendix C.

During the work-up testing, the operating protocol for the performance test was developed. Specific operating parameters including operating temperature and feed dilution were evaluated. The selection of operating parameters (feed dilution and temperature) was driven mainly by the observed physical performance of the process (pressure, temperature and flow rates), since the time for analytical feedback would have caused significant delay.

Based on the work-up testing, it was determined that a water flush of the WAO system was required for five minutes every hour to minimize the buildup of solids in the reactor inlet. Section 5.2 contains a complete discussion of the work-up testing and the rationale behind the selection of the operating protocol; the following paragraphs summarize the resulting operating protocol.

During the eight-hour performance test, the system operated with a water flush every hour. During this flush the unit was switched from simulant feed to water for a five-minute period. After the flush was completed, the simulant feed was reestablished, by adjusting the feed valve lineup. Observation of the system temperatures and pressures indicated that the water flush had little impact on the system operating parameters.

The effluent was collected and weighed on half-hour intervals. A sample was collected of the effluent every half-hour and composited. Zimpro retained these samples.

The sampling subcontractor (ENSR) collected samples twice during the 8-hour performance test. Liquid effluent, feed, and gas samples were collected for independent analysis twice during the second and sixth hours of the performance tests period. The gas samples were obtained directly from the effluent off-gas flow. The liquid effluent sample was taken from the total collected effluent during the one-hour sampling interval.

At the completion of the scheduled performance test, Zimpro, at the request of Stone & Webster, continued to operate the WAO process for an additional four-hours without the flush. The unit operated under the same procedures as the performance test, with the exception that no independent samples were collected.

All residuals and unused feed not used for analytical samples were collected for disposal at a licensed incineration facility at a later date.

4.4 Test Procedure – Post Oxidation

A portion of the liquid effluent sample collected during the performance test sampling periods (hours 2 and 6), was consolidated and used as feed to the bench-scale UV/O_3 test apparatus. The post oxidation process consisted of oxidation with ozone (O_3) and ultra-violet light (UV) in a bench scale reactor as described in Section 3. The WAO effluent liquid contained a high concentration of dissolved carbonate that was removed prior to treatment with ozone and ultraviolet light. The removal of the dissolved carbonate was necessary based on the bench-scale testing conducted previously[8]. The effluent liquid was pH adjusted with hydrochloric acid and placed in a gas sparging apparatus to remove the carbon dioxide. After the carbon dioxide was removed, the pH was adjusted with caustic and placed in the reactor. The UV oxidation process was conducted by filling the reactor with 0.7 liters of WAO effluent liquid. The test was started with the sparging of O_3 through the WAO effluent liquid. The UV bulb was switched on immediately after the first addition of the chemical oxidant. The dosage of O_3 was applied over the total duration of the test. At the conclusion of the test, the flow of O_3 gas was terminated, and the UV bulb switched off. The treated effluent was removed from the reactor and collected in a consolidated sample for analysis.

5. Test Results & Discussion – WAO

The following section discusses the results of the work-up and performance. Included are discussions of the work-up and performance testing (Sections 5.1 and 5.2, respectively). Section 5.3 and 5.4 are summaries of the analytical results. Section 5.5 is a discussion of the overall performance and operability of the WAO system.

5.1 WAO Work-up Testing

Work-up testing commenced on November 12, 2001 and continued through November 14, 2001 and included a series of continuous flow pilot WAO work-up tests to determine the operating procedures and conditions for the particular WAO unit. The basic operating parameters of temperature and residence time were based on the previous bench-scale testing. Zimpro was confident that the destruction criterion of 99.9% destruction of the relevant compounds was achievable when the process was operated within the range of 300 to 320^{o}C with a 60-minute residence time. The focus of the work-up testing was to establish the specific operating conditions that would allow operation at maximum continuous flow for the 8-hour test period.

Initially, Zimpro intended to process a 20:1 dilution of the H neutralent simulant at 320 ^{o}C for 60 minutes. After several hours of operation, the pressure drop between the oil heater outlet and reactor top increased from 10 - 20 psi to values as high as 300 - 400 psi. Zimpro's normal procedure when a pressure drop buildup occurs is to switch from organic feed to water in an attempt to dissolve the blockage. The pilot unit feed was shifted to pure water and in several minutes the restriction was removed and the pressure drop returned to normal (10 - 20 psi). This increase in pressure drop reoccurred several times over the next 5 hours. Each time the blockage could be removed by several minutes of operation on water.

This phenomenon was thought to be caused by carbonate salt precipitating from the liquid phase at the reactor inlet. Previous studies have indicated that at temperatures in excess of 300 ^{o}C, many sodium salts start to exhibit an inverse solubility as temperature increases. Zimpro operated the WAO process at a pH of 10 (at the reactor outlet) to control corrosion. This required that the feed material contained 11% caustic (by weight) to react with the acid forming components including Cl, S, and CO_2. These materials would all form their respective sodium salts, which contribute to the dissolved salt concentration. Based on the reaction chemistry, sodium carbonate (Na_2CO_3) would be the predominant salt, present at levels from 10 to 12%. While specific data on the solubility of sodium carbonate at these high temperatures is scarce, Zimpro believes that the carbonate was precipitating and causing the pressure buildup.

Zimpro's initial reaction was to adjust the operating conditions to allow operation at steady state for the performance test. Their plan was to initiate a series of parametric tests to evaluate the influence of feed concentration (dilution factor) and operating temperature on system salt precipitation as indicated by pressure drop buildup. The work-up test plan including the variable and set process parameters is shown in Table 5-1.

Table 5-1 WAO Process Work-up Testing Variables

Process Parameter	Value
Reactor outlet temperature	$300^{o}C$ - $320^{o}C$ [$572^{o}F$ - $608^{o}F$]
Reactor pressure	3,200 psig
Offgas residual oxygen concentration	5%
Nominal liquid residence time	60 minutes [1 hour]
Feed liquid	H neutralent simulant
Dilution Ratios	1 part simulant to 20 parts water 1 part simulant to 25 parts water 1 part simulant to 30 parts water

A plan was developed to conduct the tests as designated in Table 5-2 to evaluate system operation and overcome the plugging problems. The plan was to proceed down the list and once the pressure drop buildup was controlled, Zimpro would begin the performance test. The initial work-up test run was designated as test number 1.

Table 5-2 WAO Conditions Tested in Work-up Runs

Simulant	Run #	Dilution	Reactor Outlet Temperature	Nominal Liquid Residence Time	Water Wash
H Neutralent Simulant	1	20:1	320 ^{o}C	60 minutes	None
	2	25:1	320 ^{o}C	60 minutes	None
	3	30:1	320 ^{o}C	60 minutes	None
	4	30:1	320 ^{o}C	60 minutes	None
	5	30:1	300 ^{o}C	60 minutes	5 minutes/hour

Work-up Tests No. 2 and 3 were conducted at successively higher dilutions of simulant in order to reduce the concentration of sodium carbonate in the process liquid following oxidation. The same pressure excursions occurred in work-up test No. 2 with a feed consisting of 1 part simulant diluted with 25 parts water. Work-up test No. 3 was not completed due to a failure of the pressure control valve (located between the effluent cooler and gas separator) seat gasket followed soon thereafter by a failure of the reactor top gasket. Both of these failures were due to incompatibilities of the gasket materials with the operating conditions. The appropriate PCV gasket was replaced in the system. The reactor top gasket was removed and the filler material in the gasket was found to have failed. The gasket manufacturer was contacted and supplied a gasket constructed with a filler material resistant to attack at the high temperature and pH. The reactor gaskets exhibited problem free operation for the remainder of the testing.

The WAO system was out of commission for approximately 24 hours waiting for the replacement head gaskets to be delivered. During this downtime, an additional pressure transducer was installed at the reactor inlet (PT 154). This was installed to enable the operators to further isolate the location of the blockage.

Work-up test No. 4 was a repeat of work-up test No. 3 and was conducted after the gasket replacements. The high-pressure drop between the oil heater outlet and the reactor inlet was again noted. With the newly located pressure sensor (PT-154) at the reactor bottom, it was determined that the deposits were most likely occurring in the line several inches prior to the reactor. In all cases, a water rinse would remove the blockage in several minutes. The pilot unit was operated for a 2½-hour period with intermittent water rinses. Each water rinse was for a several minute duration. A second failure of the PCV gasket material occurred at the conclusion of the test period. Upon examination, it was determined that the previously installed PCV seat gasket was not of the type indicated on the packaging and not suitable for the pH of the system. A new seat gasket was installed and testing continued.

During test No. 5, the reactor temperature was reduced to 300°C (572°F). The purpose was to operate at a slightly lower temperature to increase the solubility of the sodium carbonate. The operational procedures were revised to include a preventative maintenance water flush to be conducted for 5 minutes each hour. During the preventative maintenance water flush, the pilot unit was switched from neutralent simulant feed to water. This action was expected to remove any deposits of sodium carbonate and allow operation for the remainder of the hour without any pressure drop excursions.

Based on the success of operation with the intermittent rinsing, Zimpro set the performance test conditions as 300 °C for 60 minutes with a 5-minute water rinse every hour.

5.2 WAO Performance Testing

At 0800 hours on November 15, 2001 the performance test was initiated. The testing followed the procedures outlined in Appendix C and a timeline and summary sheets/plots are included in Appendix D. WAO liquid and offgas effluents were sampled two times during the 8-hour performance test, once during the second hour (0900) and another during the sixth hour (1300). Each sampling period included a 5-minute water rinse cycle. In addition, the simulant feed material was analyzed during each sampling period.

Table 5-3 is a summary of the performance test operating conditions.

Table 5-3 Performance Test Summary – H neutralent simulant

	Planned	Actual
Reactor Temperature	300 °C	299 °C
Reactor Pressure	3,200	3,211 psig
Nominal Liquid Residence Time	60 minutes	60 minutes
Offgas Oxygen	5%	7.3 %
Simulant Flowrate	6.4 gal/hr	6.4 gal/hr
Rinse Water Flowrate	0.6 gal/hr	0.6 gal/hr
Dilution Ratio	30:1	30:1
Water Flush Sequence	5 minutes every hour	5 minutes every hour

The performance test was operated at a reactor top temperature of 300°C (572°F), with a feed liquor consisting of 1 part simulant to 30 parts dilution water. Figure 5-1 shows the stability of the temperature over the performance test. Note that the small deviation (approximately 4^{o}C) is due to the water rinse cycles. Figure 5-2 is a plot of the differential pressures. Although there were several random spikes, no significant pressure drop excursions were noted during the 8-hour test.

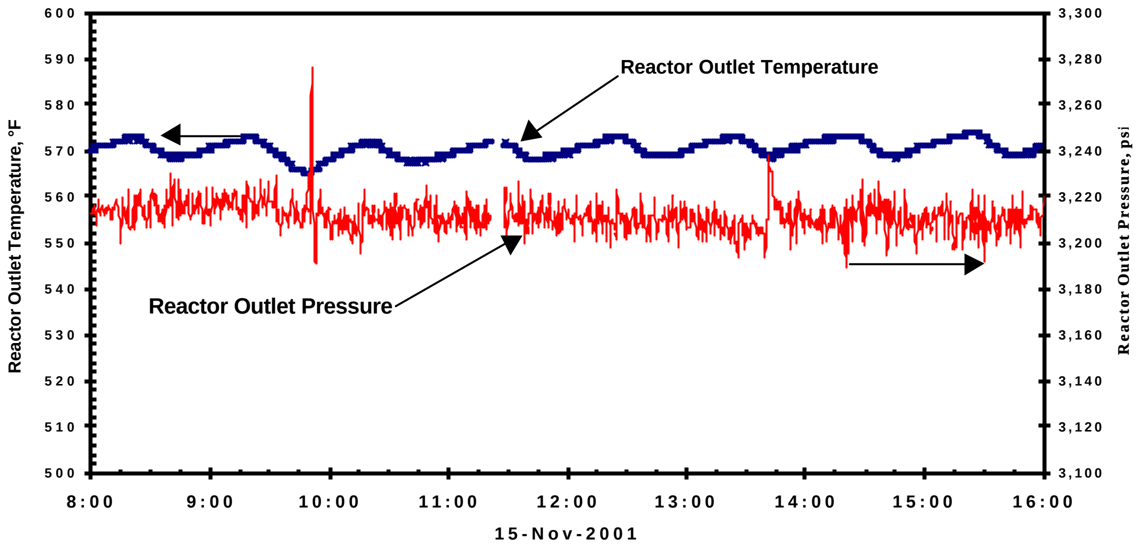

Figure 5-1 WAO Reactor Outlet Temperature and Pressure during Performance Test

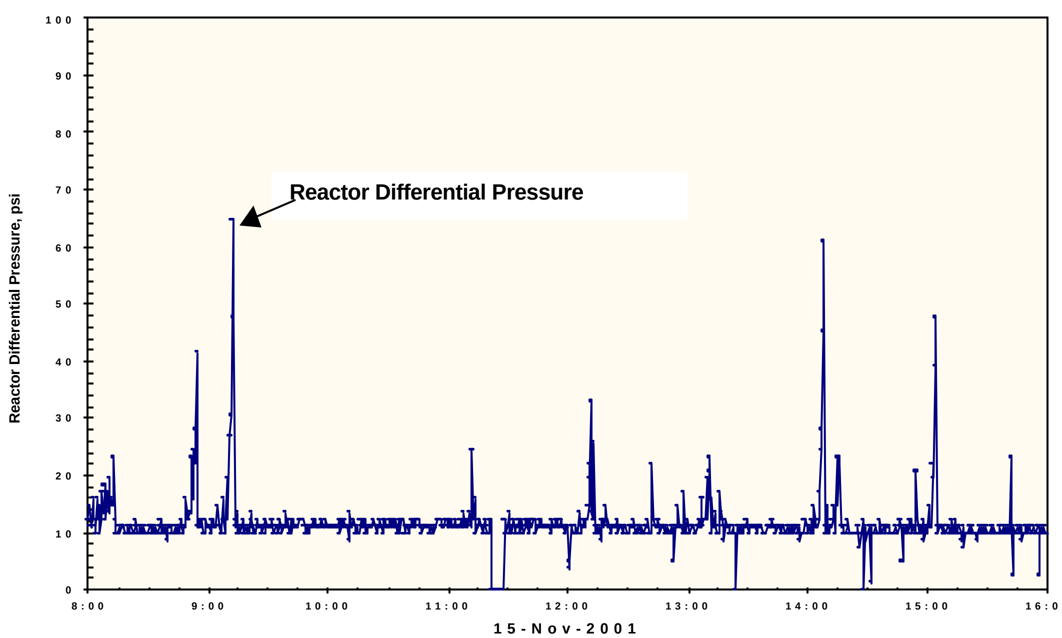

Figure 5-2 Differential Pressures during Performance Test

Airflow was maintained by presetting a needle valve, and the residual oxygen was monitored continuously downstream of the gas separator. Figure 5-3 shows several interesting transients. There are periodic increased in offgas oxygen concentrations that coincide with the water rinses. In addition, there are two additional transients at approximately 0930 and 1330. Apparently a particle of dirt or dust became lodged in the needle valve used to control the airflow and the valve had to be cycled to clear the obstruction. Figure 5-4 is a photograph of the control valve indicating its size relative to a finger. This plugging should be avoided in a full-scale unit with a larger control valve.

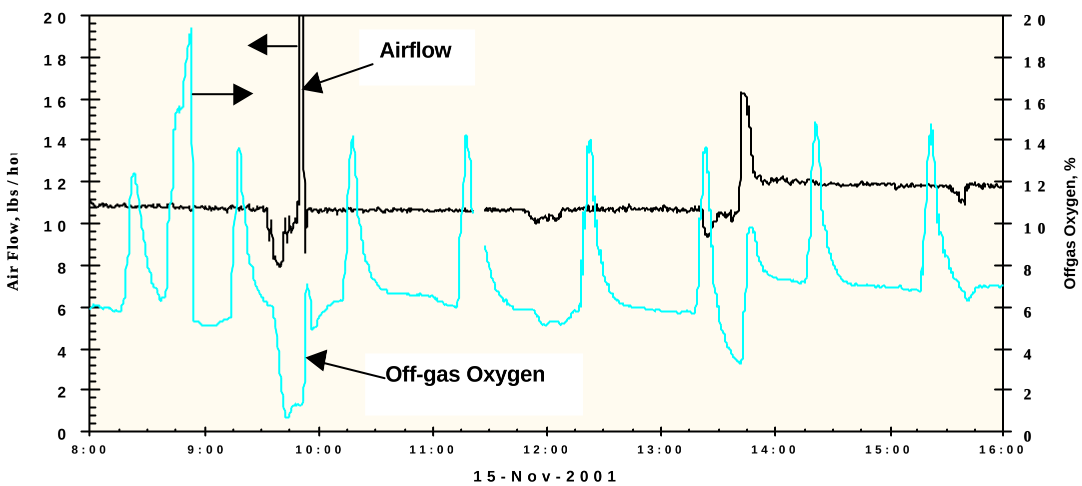

Figure 5-3 Airflow and Off-gas Oxygen during Performance Test

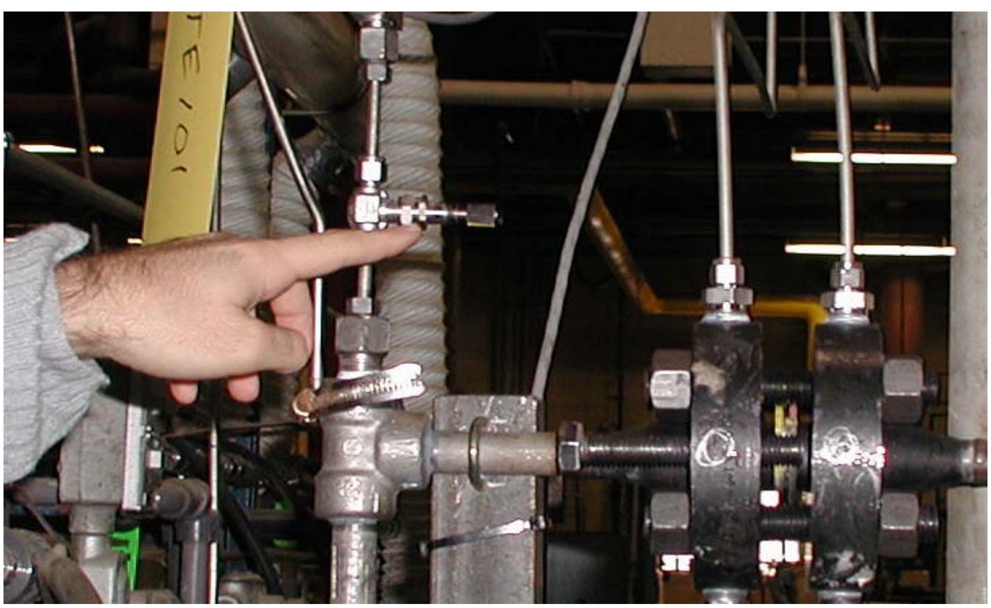

Figure 5-4 Pilot Plant Airflow Control Needle Valve

This document was prepared under contract with the United States Army for the sole purpose of evaluating the identified technology for potential application in the United States Army Chemical Demilitarization Program (CDP), based on information available to the reviewer at the time of the evaluation. Any opinions, findings, recommendations or conclusions expressed are stated in the context of the particular considerations of the CDP, and are not intended for use or reference in any way by any other party for any other purpose.

5.2.1 WAO Performance Test Extension

Upon the completion of the performance test, Zimpro continued operation of the system for an additional 4-hours without water rinses to observe system performance. During the period, the WAO reactor inlet experienced several instances of pressure buildup that were spontaneously eliminated either by washout or dissolution. Figure 5-5 is a plot of the differential pressure over the reactor during the performance test extension. Although no samples were taken during this period, temperature and airflow were maintained as shown in Figure 5-6 and one would expect destruction levels to be maintained.

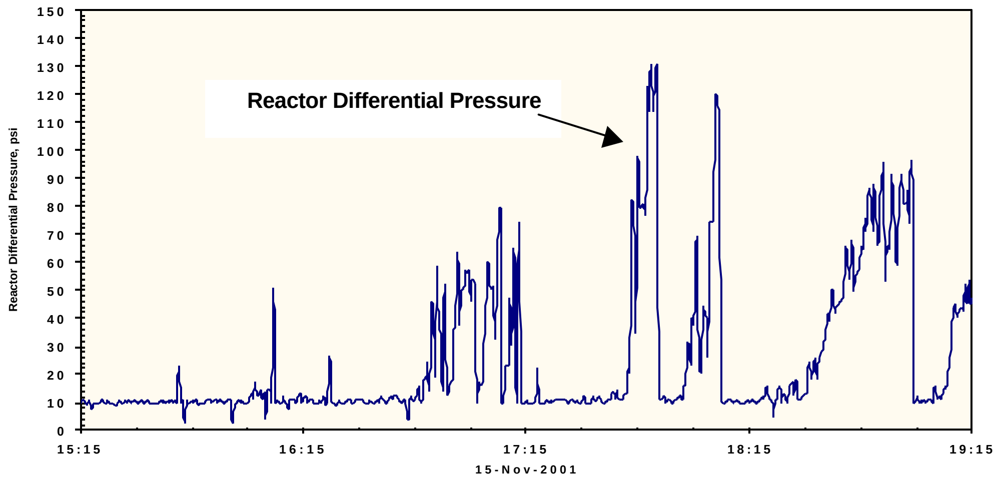

Figure 5-5 Differential Pressures during Performance Test Extension

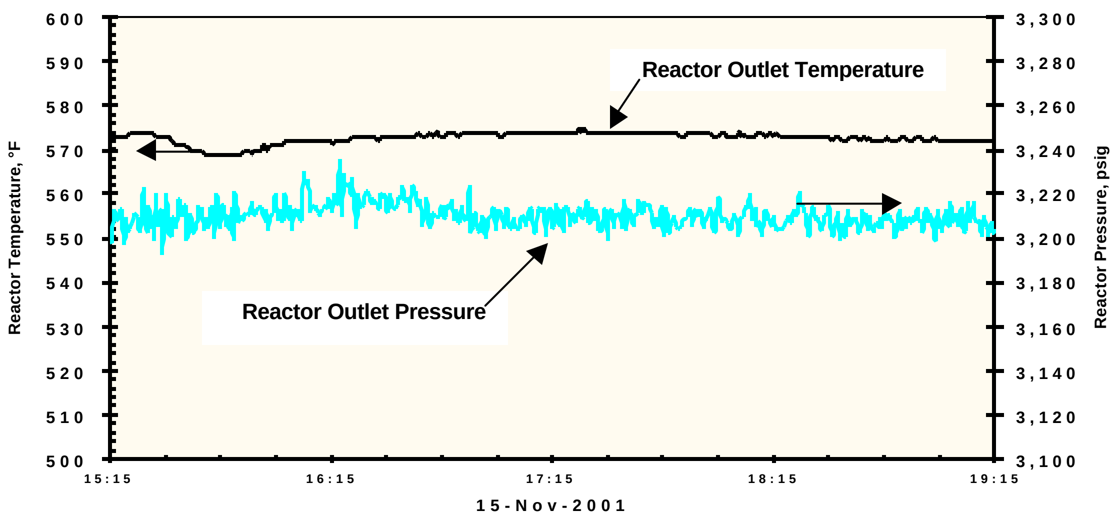

Figure 5-6 WAO Reactor Outlet Temperatures and Pressure During Performance Test Extension

5.3 Effluent characteristics

Effluents from the performance test were collected and analyzed in accordance with the Sampling and Analysis Plan. The results reported herein are based on the reports received from the analytical subcontractors ENSR[9] and SwRI[10]. Copies of the summary reports are included in Appendix A and Appendix B of this report.

5.3.1 Gases

The evolved gases from the performance test were sampled by ENSR two times during the performance test at 0900 and 1300 hours. The gas samples were collected over a one-hour period in midget impingers, Tedlar™ bags, or XAD resin tubes. Permanent gases were sampled and tested by an online Enerac Analyzer. The individual analysis results along with collection methods are described in Sections 5.3.1.1 through 5.3.1.5. The samples collected in the Tedlar bags and resin tubes were then sent to PSC (formerly Philips Analytical Services) for analysis unless noted otherwise.

5.3.1.1 Permanent Gases, Carbon Monoxide, and Nitric Oxides

These analyses were performed for O_2, CO_2, NO_x, and CO in accordance with EPA 3A, 7E and 10 (Rev1/Sep 00) with an Enerac portable multi-component analyzer (chemical cells for detection). The portable multi-component analyzer was calibrated at two points for each parameter at the zero level and upscale calibration utilizing EPA protocol gases. During the course of each 1-hour sample collection, three instantaneous readings were collected and averaged to calculate the concentration. After the three measurements are complete, the analyzer calibration was checked for drift. Table 5-4 presents gas concentrations measured in the samples.

Table 5-4 WAO Process Permanent Gases and Carbon Monoxide Results

Sample Time	CO2 (%)	O2 (%)	NO_x (ppm)	CO (ppm)
Hour 2	0.0	6.5	1.0	2.0
Hour 6	0.0	7.4	2.4	3.2
Average	0.0	7.0	1.7	2.6

5.3.1.2 Inorganic Gas Analysis

The analytical results of the gases collected in the midget impingers for various inorganic analytes are presented in Table 5-5.

The analytes sampled and corresponding methods included sulfur oxides (SOx) -EPA Method 6; chlorine (Cl_2) -EPA method 0050; hydrogen chloride (HCl) -EPA method 0050; and ammonia (NH_3) -EPA method CTM-027. The gases within the midget impingers were extracted through the appropriate filters, sorbent tubes, or impinger solutions as detailed in the Sampling and Analysis Plan. The samples were sent to the analytical laboratory for analysis by ion chromatography.

Table 5-5 WAO Inorganic Gas Analyses

Sample Time	Mass of Compound detected (mg/m^3)			
	SO_x	Cl_2	HCl	NH_3
Hour 2	1.61	< 0.50	< 1.25	8,213
Hour 6	1.62	< 0.50	< 1.25	11,480
Average	1.62	< 0.50	< 1.25	9,846

5.3.1.3 Gas Analysis for Semi-Volatile Organic Compounds

Semi-volatile organic compounds were collected in accordance with the general procedures outlined in EPA Method 18, sorbent tube procedure. The sampling train consisted of a Teflon probe, an empty impinger to knockout moisture, two XAD tubes connected in series, and a personal monitoring pump calibrated at a flow rate of 500 cc/min. At the completion of each sampling run, the XAD tubes were capped, labeled and shipped to the analytical laboratory for GC-MS analysis. Back to back sample tubes were analyzed separately as a check on analyte breakthrough. The analyses looked for specific compounds that are listed in the analytical report contained in Appendix A and Appendix B. There were no semi-volatile organic compounds present above the analytical detection limits. The detection limits for these analyses ranged from 200 to 265 ug/m^3, and are noted in the Appendices.

5.3.1.4 Gas Analysis for Volatile Organic Compounds

Sample gases collected in Tedlar™ sample bags were analyzed for their VOC content using EPA Method 18. Sampling was completed by use of a "lung" type sampling system. In this procedure, the Tedlar™ bag is connected to the offgas sampling line via a Teflon probe and placed in a sealed, rigid container. The container was evacuated at a flow rate of 300cc/min, as the pressure inside the container decreased, the bag fills with sample gas at the same rate as the evacuation rate. Condensate was collected from the impinger for the second sample period and was analyzed along with the Tedlar bag for volatile organics.

Table 5-6 presents a listing of the compounds detected during the VOC analyses. The analyses looked for specific compounds that are listed in the analytical report contained in Appendices A and B as the target compounds specified by the EPA Method 18 that are positively identified by the method protocol.

Detection limits for the analyses ranged from 40 to 170 ppbv. The summary table indicates that two compounds were detected in the residual gas. These compounds detected are present at very low quantities and are not expected to pose a problem to permitting a system.

Table 5-6 Volatile Organic Compounds Detected in WAO Off-gas Samples

	Concentration (ppb)	
Compound	Sample (hr 2)	Sample (hr 6)
Dichloromethane	500	< 100
1,2,4-trichlorobenzene	130	< 80

5.3.1.5 Gas Analysis for MEA and Carbon-Sulfur (C-S) Bonds

The analytical results of the gases collected in the midget impingers for MEA and C-S bonds are presented in Table 5-7. The sampling train included the first two impingers with 15 mL of deionized water, the third impinger remained empty, and the fourth contained silica gel. Effluent gases were drawn through a heated probe, a glass fiber particulate filter, and impingers at a rate of 1 liter/min for sixty minutes. At the conclusion of the test, the impingers were collected and rinsed with DI water into a glass sample jar and sent to the laboratory for analysis.

Table 5-7 MEA and C-S Bonds Detected in WAO Off-gas Samples

Sample Time	Concentration	
	MEA (ppm)	C-S Bonds (%)
Hour 2	2.0	< 0.5
Hour 6	< 1.0	< 0.5

5.3.2 Liquid Effluents

The WAO liquid effluents from the performance test were sampled by ENSR two times during the performance test. The two 1-hour test runs were conducted at 0900 and 1300 hours of the 8-hour test run to assess the WAO performance over time. During the sample periods a procedural water rinse was conducted for 5 minutes of the collection period. The processed liquid from the entire hour of operation and samples were collected from this consolidated material. The liquid sample analysis results are described in Sections 5.3.2.1 through 5.3.2.6. The samples were then sent to PSC (formerly Philips Analytical Services) for analysis unless noted otherwise.

5.3.2.1 Liquid Analyses for Volatile Organic Compounds

Volatile Organic Compounds (VOC) were analyzed by EPA method 8260B by both ENSR (through PSC) and SwRI. The samples at SwRI were analyzed as received through direct injection into the GC/MS with a detection limit of 1 ppb. The direct injection method used by SwRI expanded the compounds screened.

ENSR (through PSC) used a purge and trap (Method 5030/5035) that limited the number of analytes. PSC also performed an additional dilution based on the pH of the sample and reported based on detection limits ranging from 8 to 250 ppb.

Table 5-8 lists only the compounds that were detected by either ENSR or SwRI. The entire listing of compounds analyzed and detection limits are contained in the analytical reports in Appendix A and B.

Table 5-8 Detected Volatile Organic Compounds in WAO Liquid Effluent

	Concentration (ppb)			
	Sample (hr 2)		Sample (hr 6)	
Compound	**ENSR**	**SwRI**	**ENSR**	**SwRI**
Acetone	<250	**36**	<250	**48**
Bromomethane	<20	**62**	<20	**15**
Carbon Disulfide	<18	**1.5**	<18	**1.4**
Carbon oxide sulfide	N/A	< 1.0	N/A	**1000**
Chloromethane	<28	**580**	<28	**270**
Diethyl disulfide	N/A	**200**	N/A	**40**
Ethyl ester thiocyanic acid	N/A	< 1.0	N/A	**9**
2-Hydroxypropanamide	N/A	**50**	N/A	< 1.0
Methoxy acetic acid	N/A	< 1.0	N/A	**9**
Methyl ester thiocyanic acid	N/A	< 1.0	N/A	**9**
Methyl ethyl disulfide	N/A	< 1.0	N/A	**2**
2-Propanamine	N/A	**50**	N/A	< 1.0
Propanol	N/A	< 1.0	N/A	**9**
Vinyl Chloride	< 18	**1.3**	< 18	**2.1**

N/A = not included in the analysis

5.3.2.2 Liquid Analyses for DMSO, MSA, and C-S Bonds

SwRI analyzed the WAO liquid effluent for dimethyl sulfoxide (DMSO), methyl sulfonic acid (MSA), and Carbon-Sulfur (C-S) bonds. DMSO is of particular concern as a representative of the C-S bonds that are present in NSCMP mustard and neutralent materials. In addition to DMSO, the liquid effluent was analyzed for MSA, the intermediate oxidation product of DMSO, to evaluate the WAO process' ability to effectively destroy these compounds. The samples were analyzed using SwRI's internally developed GC/MS protocols.

As noted in Table 5-9, the levels of DMSO, MSA, and C-S bonds were all below the detection limits for the particular analyses. The resulting destruction efficiencies are discussed in Section 5.4.1 and summarized in Table 5-13.

Table 5-9 WAO Effluent DMSO, MSA and C-S Bond Analyses

Compound	**Sample (hr 2)**	**Sample (hr 6)**
Dimethyl sulfoxide, DMSO (ppm)	< 0.10	< 0.10
Methyl sulfonic acid, MSA (ppb)	< 10	< 10
C-S Bonds (%)	< 0.5	< 0.5

5.3.2.3 Liquid Analyses for Semi-Volatile Organic Compound

All of collected samples were analyzed for semi-volatile organic compounds utilizing EPA method 8270. Sixty-nine compounds were analyzed with a minimum detection level below 5.0

micrograms-per-liter (ppb). The entire listing of compounds analyzed and detection limits is contained in the analytical report in Appendix B.

Two compounds (Benzyl butyl phthalate and Bis (2-ethylhexyl) phthalate) were detected in one sample at levels of less than 2 ppb. These materials are thought by the laboratory to be contaminants introduced by plastic materials in the sampling train or detection instrumentation. There were no semi-volatile organic compounds present above the analytical detection limits. The detection limits for these tests ranged from 0.2 to 4.8 ppb, and are noted in Appendix A.

5.3.2.4 Liquid Analyses for Dioxins and Furans

The WAO effluent was analyzed for dioxins and furans by EPA method SW846-8290. Table 5-10 presents the components detected in the samples as well as the blank.

Table 5-10 WAO Effluent Dioxin and Furan Analyses

Component	Concentration (parts-per-trillion)		
	Method Blank	Hour 2	Hour 6
Total Tetrachlorodibenzofurans	<1.1	<1.2	<0.82
Total Pentachlorodibenzofurans	<0.98	<0.98	<1.1
Total Hexachlorodibenzofurans	<1.1	<0.99	<0.86
Total Heptachlorodibenzofurans	<1.4	<1.2	<1.3
Octachlorodibenzofuran	5.4	8.6	5.4
Total Tetrachlorodibenzo-p-dioxins	<1.1	1.8	<3.5
Total Pentachlorodibenzo-p-dioxins	<1.5	<1.8	<1.6
Total Hexachlorodibenzo-p-dioxins	2.2	<1.9	<2.6
Total Heptachlorodibenzo-p-dioxins	<2.7	<1.4	<1.3
Octachlorodibenzo-p-dioxin	<3.1	11	1.6
2,3,7,8-Cl4-Dibenzofuran (DB5)	<1.1	<1.2	<0.82
2,3,7,8-Cl4-Dibenzo-p-dioxin	<1.1	<1.4	<1.0
1,2,3,7,8-Cl5-Dibenzofuran	<0.95	<0.94	<1.1
2,3,4,7,8-Cl5-Dibenzofuran	<1.0	<1.0	<1.2
1,2,3,7,8-Cl5-Dibenzo-p-dioxin	<1.5	<1.8	<1.0
1,2,3,4,7,8-Cl6-Dibenzofuran	<0.95	<0.84	<0.73
1,2,3,6,7,8-Cl6-Dibenzofuran	<0.99	<0.87	<0.76
2,3,4,6,7,8-Cl6-Dibenzofuran	<1.2	<1.1	<0.96
1,2,3,7,8,9-Cl6-Dibenzofuran	<1.4	<1.3	<1.1
1,2,3,4,7,8-Cl6-Dibenzo-p-dioxin	<1.7	<1.1	<1.1
1,2,3,6,7,8-Cl6-Dibenzo-p-dioxin	2.2	<1.0	<1.0
1,2,3,7,8,9-Cl6-Dibenzo-p-dioxin	<1.5	<0.98	<1.00
1,2,3,4,6,7,8-Cl7-Dibenzofuran	<1.2	<1.3	<1.1
1,2,3,4,7,8,9-Cl7-Dibenzofuran	<1.7	<1.5	<1.6
1,2,3,4,6,7,8-Cl7-Dibenzo-p-dioxin	<2.7	<1.4	<1.3
1,2,3,4,6,7,8,9-Cl8-Dibenzofuran	5.4	8.6	5.4
1,2,3,4,6,7,8,9-Cl8-Dibenzo-p-dioxin	<3.1	11	1.6

5.3.2.5 Metal Analyses

The metal analyses of the treated liquid residue samples utilizing EPA method SW846 6110B are presented in Table 5-11.

Table 5-11 WAO Liquid Effluent Metal Analyses

	Concentration (parts-per-million)		
Element	**Sample (hr 2)**	**Sample (hr 6)**	**Average**
Aluminum	1.3	1.3	1.3
Barium	0.033	0.016	0.025
Beryllium	<0.010	<0.010	-
Cadmium	<0.020	<0.020	-
Calcium	6.6	6.8	6.7
Chromium	11	15	13
Cobalt	<0.010	<0.010	-
Copper	0.22	0.23	0.23
Iron	4.3	4.6	4.5
Lead	0.41	0.29	0.35
Magnesium	2.4	2.2	2.3
Manganese	<0.060	<0.060	-
Molybdenum	0.13	0.21	0.17
Nickel	2.0	2.2	2.1
Phosphorus	<0.060	<0.060	-
Potassium	47	41	44
Silver	<0.050	<0.050	-
Sodium	31,000	31,000	31,000
Thallium	<0.60	<0.60	-
Vanadium	0.060	0.050	0.055
Zinc	0.20	0.13	0.17

5.3.2.6 Anion Analyses

The liquid samples were also analyzed for anion concentrations using the ion chromatographic EPA Method SW-846 9056. Results of these analyses are presented in Table 5-12.

Table 5-12 Anion Analyses of WAO Liquid Effluent

	Concentration (parts-per-million)		
Compound	**Sample (hr 2)**	**Sample (hr 6)**	**Average**
Chloride	320	340	330
Nitrite	540	600	570
Nitrate	73	79	76
Sulfite	< 10	< 10	-
Sulfate	450	480	465

5.3.3 Solids

There were no solids generated during the WAO performance testing of the H neutralent simulant.

5.4 Destruction Efficiencies

A material balance was performed on the system to evaluate both destruction efficiency of the process and determine the fate of specific compounds.

5.4.1 Organic Carbon Destruction Efficiency

The destruction efficiency of the WAO process was determined based on the TOC of the diluted feed and effluents. This method determines the actual destruction observed in the WAO system and does not include any credit gained by dilution of the feed. The initial TOC is determined by the simulant formulation. The effluents include the offgas and the liquid exiting the liquid/vapor separator. The destruction efficiency is simply the difference between the initial and final quantity of TOC divided by the initial amount of TOC.

In all performance test cases, the residual organic carbon in the vapor did not impact the amount of residual carbon. In the case of the liquid residual, the TOC analyses were used to determine the destruction efficiencies noted in Table 5-13.

5.4.2 C-S Bond Destruction

The H neutralent simulant performance test was evaluated based on the destruction of the DMSO. In addition, the destruction of the C-S bonds was measured as the initial number of C-S bonds (molar concentration of DMSO in the dilute feed) compared to the number of C-S bonds remaining after WAO treatment (molar concentration of MSA).

The results of the C-S bond destruction calculations are summarized in **Table 5-13**.

Table 5-13 WAO Performance Tests Destruction Efficiencies

	Initial Concentration (ppm)	**Sample (hr 2)**		**Sample (hr 6)**	
		Residual (ppm)	Destruction (%)	Residual (ppm)	Destruction (%)
Total Organic Carbon, TOC	11,726	295	97.48	276	97.65
Chemical Oxygen Demand, COD	68,915	1,300	98.11	1,800	97.39
Dimethyl sulfoxide, DMSO	968	< 0.1	> 99.99	< 0.1	> 99.99
Methyl Sulfonic Acid, MSA	---	< 0.01	> 99.999	< 0.01	> 99.999

Initial concentrations based on diluted feed
All reductions shown as ">" are based on calculations using the minimum detection limit as the final concentration
MSA destruction based on C-S bonds

5.4.3 Specific Organic Compound Destruction

An analysis of the residual liquid was conducted to evaluate the destruction efficiency of the major organic constituents in the simulant. Table 5-14 presents these results.

Table 5-14 WAO Performance Test Organic Destruction Efficiencies

	Initial Concentration (ppm)	Sample (hr 2)		Sample (hr 6)	
		Residual (ppm)	Destruction (%)	Residual (ppm)	Destruction (%)
Dimethyl sulfoxide, DMSO	968	< 0.1	> 99.99	< 0.1	> 99.99
Methyl Ethanolamine, MEA	26,774	2.0	99.99	< 1.0	> 99.99
Dichloroethane, DCE	1,258	< 0.001	> 99.9999	< 0.001	> 99.9999

Initial concentrations based on diluted feed

All reductions shown as ">" are based on calculations using the minimum detection limit as the final concentration

5.5 Operability

The WAO pilot-scale unit generally operated well once the operating protocol of hourly rinsing was established. The only processing deviations were associated with the plugging of the air control valve, which is attributed to the scale of the pilot unit equipment and should be avoided in a full-scale facility.

Testing was conducted on the pilot-scale system, with equipment and operations, similar to a full-scale system. While the unit did incorporate many of the features that would be a part of a full-scale system, there were some differences. These are discussed in the following section while the features of a full-scale processing concept are discussed in Section 8.

5.5.1 System Operation

The WAO system operation was straightforward. The feed was prepared (diluted and caustic added) in a mix tank and transferred to a smaller feed tank. The feed tank provided suction to a low-pressure recycle pump that provides suction pressure to a high-pressure feed pump. The feed was preheated using hot oil as the heat source, which is a deviation from typical large-scale WAO applications. In most commercial applications, the feed is preheated against the effluent. However given the size of the intended NSCMP application, Zimpro proposes to use a steam or hot oil as a heat source for preheating, and cooling water on the WAO reactor effluent. This method is used by Zimpro in smaller commercial applications and allows better control of the system.

The reactor was heated to 250 ^{o}C with water flow. This generally took about four-hours then the diluted simulant feed was introduced and the oxidation of the organic matter brought the system up to operating temperature (300^{o}C) within two hours. After approximately four hours the system was stable and operating at steady state.

The hourly rinse was accomplished by switching two valves at the inlet to the high-pressure pump. This was done manually, although would be automated in the full-scale system.

5.5.2 Plugging/Water Rinses

The operating procedure for the WAO unit included a 5-minute rinse with clean water every hour. This was not originally planned, but rather a response to observed plugging during the work-up testing. The system worked well with the hourly rinse, and the procedure to initiate it was simple. Figure 5-1 shows that the temperature in the reactor remained within 4 ^{o}C of setpoint during the rinse cycle. All samples taken included a rinse cycle and demonstrated satisfactory overall destruction efficiency.

Following the performance test, the system was operated for an additional 4-hours with no rinsing to evaluate system operation. This performance test extension is discussed in Section 5.2.1 and indicated that although several pressure buildups were observed, they were self-clearing. Although the 4-hour test is not indicative of long-term operational viability, it does indicate that there is the potential to eliminate the rinsing and its associated reduction in throughput.

While the water rinses apparently solved the observed plugging for this feed material, the bench-scale autoclave study[11] indicated that higher temperatures are required to effectively break the C-P bond that is present in some CWC Schedule compounds. The plugging was observed to occur as temperature reached and exceeded 300°C, and the bench testing indicated operation at 320°C was required to break the C-P bond. Further testing at the pilot-scale is necessary to determine if plugging is observed with the other feeds. In the event plugging is observed, alternative operating modes should be evaluated including intermittent rinsing or operation at a neutral pH to reduce the concentration of sodium carbonate present.

5.5.3 Valving

The WAO pilot plant experienced several valve problems during the work-up testing. The pressure control valve seat gasket failed twice. Analysis after the second failure indicated that the previously used gasket material was mislabeled and the proper gasket material was installed and operations continued without further incident.

The air control needle valve was obstructed twice during the performance test. This needle valve was preset to regulate the airflow to the system. The installed valve (shown in Figure 5-4) is approximately one-half-inch in size and more of a laboratory device. A full-scale application would have a larger valve, and thereby avoid the problem.

5.5.4 Instrumentation

Instrumentation in the WAO system included standard temperature sensors and pressure transducers installed at various locations as shown in Figure 3-1, the pilot plant process flow diagram. Standard sheathed temperature sensors are used and both the pressure and temperature sensing devices have been used extensively in the field.

Additional instrumentation included a continuous oxygen monitor and flowmeter installed in the gas effluent line. Both items are standard commercial equipment. Additional monitoring devices could be installed in the gaseous effluent lines as required by the specific application.

5.5.5 Control and Data Acquisition

A computer monitored all operations and collected operating data. In general reactor temperature and pressure controller setpoints were manually set and remained as initially set throughout the operation. This is indicative of full-scale operations since the WAO units are designed to process feed mixtures with a defined range of variation. The reactor temperature and pressure controllers will respond to changes in process parameters as the feed composition varies to maintain the proper reactor temperature and pressure. If the feed composition varies beyond the pre-defined range, the system may go into an alarm condition (through high temperature or low flow) to alert the operator to take action.

Operating parameters including temperature and pressure were recorded by the data acquisition system and used to automatically calculate flows and differential pressures through key components. Other than an on-line oxygen monitor that is used as an alarm setpoint, the pilot unit did not have on-line analytical instrumentation.

Zimpro has developed a graphic display that is used to monitor the system using a PC. The process flow is depicted, with key monitoring points noted and real-time values (direct or calculated) shown. In the pilot plant test the PC controlled reactor pressure and monitoredthe system. Temperature was controlled by a separate instrument.

5.5.6 Other

The reactor head gasket failed during the initial work-up test. Upon evaluation it was determined that the filler material in the gasket had been de-rated by the manufacturer from 600 to 575 ^{o}F, and no longer appropriate for service. Zimpro ordered and installed new gaskets with appropriate materials, and the tests proceeded. The head gaskets did not cause any problems throughout the duration of the testing.

6. Test Results & Discussion – Post Oxidation

It was originally anticipated that the WAO effluent would contain short-chain organic compounds and ammonia that would require further processing to meet the overall treatment objectives of 99.9% destruction of the subject compounds and an overall TOC of less than 25 ppm. The post-treatment options that were considered by Zimpro for the WAO effluent were biotreatment, UV Oxidation (with H_2O_2 or O_3), or a combination of both.

Based on the bench-scale testing, post treatment of the WAO effluent was evaluated using a process consisting of oxidation with ultra-violet light enhanced by the addition of ozone (UV/O_3). The same bench-scale batch apparatus was used as for the previous testing[12]. The apparatus is discussed in Section 3.2 and the operating procedures in Section 4.4.

The following section discusses the results of the UV/O_3 performance testing that was conducted in Phase IIa on the post-treatment process. Included are discussions of the performance testing (Sections 6.1) and effluent analyses/characterization (Section 6.2).

6.1 Post Oxidation Performance Test

The UV/O_3 process test was initiated following with the WAO Performance test. The two liquid samples taken during the performance test were combined and used as the feedstock for the testing. The testing followed the procedures outlined in Section 4.4. The summary of the post-treatment performance test is shown in Table 6-1.

Table 6-1 Post-treatment/UV/O_3 Performance Test Summary – H neutralent simulant

Feed Material	WAO Effluent
Pretreatment	Acidify, air purge, adjust pH to 10
Charge Volume, mL	700
Gas Flow, mL/min	500
Ozone Concentration in gas, %	3.0
Reaction Time, min	270
UV Lamp Pressure	Medium
Ozone Dosage Rate, mg/min/L	44
Total Ozone Dosage, mg/L	11,782

6.2 Post-treatment Effluent Characteristics

All effluents from the post-treatment performance test were collected, consolidated, and analyzed in accordance with the Sampling and Analysis Plan. The results reported herein are based on the report received from the analytical subcontractors ENSR[9] and SwRI[10]. A copy of the summary reports is included as Appendix A and Appendix B in this report.

6.2.1 Gases

Gas samples were not obtained during the post-treatment testing.

6.2.2 Post Treatment Liquid Residual

The liquid residual from the UV/O3 oxidation tests were consolidated and analyzed as discussed in the following sections.

6.2.2.1 Post Treatment Residual Analyses for Volatile Organic Compounds

Volatile Organic Compounds (VOC) were analyzed by EPA Method 8260B by both ENSR (through PSC) and SwRI. The samples at SwRI were analyzed as received through direct injection into the GC/MS with a detection limit of 1 ppb. The direct injection method used by SwRI expanded the compounds screened.

ENSR (through PSC) used a purge and trap (Method 5030/5035) that limited the number of analytes. PSC also performed an additional dilution based on the pH of the sample and reported based on detection limits ranging from 8 to 250 ppb. The entire listing of compounds analyzed and detection limits are contained in the analytical report in Appendix A and B.

Table 6-2 lists the specific compounds that were detected.

Table 6-2 Detected Volatile Organic Compounds in Post-treatment Effluent

	Concentration (parts-per-billion)	
Compound	**ENSR**	**SwRI**
Acetaldehyde	N/A	300
Acetic Acid	N/A	4
Acetone	160	420
Bromomethane	8.7	0.53
Butanal	N/A	30
2-Butanone	55	96
Carbon Disulfide	<0.9	2.6
Chloroethane	<0.9	0.58
Chloromethane	1.9	4.5
Dichloroethane	<0.5	0.91
Fluorotrimethylsilane	N/A	2
Heptanone	N/A	100
2-Hexanone	10	18
Methylene Chloride	<2.3	15
Propanenitrile	N/A	3
Vinyl Chloride	<0.9	0.55

N/A = not included in the analysis

6.2.2.2 DMSO, MSA and C-S Bonds

The post treatment residual was analyzed for dimethyl sulfoxide (DMSO), methyl sulfonic acid (MSA), and Carbon-Sulfur (C-S) bonds.

The WAO effluent, the UV/O3 oxidation feedstock contained less than the minimum detectable levels of these compounds, and as shown in Table 6-3 the post treatment residual also contained less than the minimum detectable.

Table 6-3 DMSO, MSA and C-S Bond Analyses Post-treatment Residual

Compound	
Dimethyl sulfoxide, DMSO (ppm)	<0.10
Methyl sulfonic acid, MSA (ppb)	<50
C-S Bonds (%)	<0.50

6.2.2.3 Anions

The post treatment residual samples were also analyzed for anion concentrations using the ion chromatographic EPA Method SW-846 9056. Results of these analyses are presented in Table 6-4. Note that the chloride concentration was present in high levels due to the preparation procedures of the UV/O_3 feed that required addition of hydrochloric acid (HCl) to adjust the pH.

Table 6-4 Anion Analyses of Post-treatment Residual

	Concentration (ppm)
Chloride	1,100
Nitrite	0.21
Nitrate	5.6
Sulfite	<10
Sulfate	250

6.2.3 Solids

There were no solids generated during the post-treatment process.

6.3 Destruction Efficiencies

The WAO process effectively destroyed the relevant compounds (DMSO, MEA, DCE, and MSA) in the simulant feed therefore the destruction efficiencies of the UV/O_3 post treatment are not an issue.

7. Combined WAO and Post-treatment Performance

The WAO system provides virtually all of the observed treatment of the simulant. Table 7-1 summarizes the overall performance of the WAO followed by UV/O_3 post treatment process.

Table 7-1 Overall Performance - H Neutralent Simulant

	H Neutralent Simulant			
	WAO Residual		Post-treatment Residual	Combined Process
	Hour 2	Hour 6		
WAO Process				
Residence Time (min)	60	60	-	
Temperature (^oC)	300	300	-	
Post-treatment				
O3 Dose Rate (mg/min/L)	-	-	44	
Reaction Time (min)	-	-	270	
UV Lamp Pressure	-	-	Medium	
Total O3 Dosage (mg/L)	-	-	11,782	
Analytical Results				
COD (ppm)	1300	1800	1300	
TOC (ppm)	295	276	295	
MSA (ppb)	<10	<10	<50	
C-S Bonds (%)	<0.5	<0.5	<0.5	
Calculated Results				
COD Destruction (%)	98.11	97.39	16.1	98.11
TOC Destruction (%)	97.48	97.65	N/M	97.65
DMSO Destruction (%)	> 99.99	> 99.99	N/M	> 99.99
MEA Destruction (%)	99.99	> 99.99	50.0	> 99.99
DCE Destruction (%)	> 99.9999	> 99.9999	N/M	> 99.9999
C-S Bond Destruction (%)	> 99.999	> 99.999	N/M	> 99.999

Initial concentrations based on diluted feed

N/M = not measurable

All reductions shown as “>” are based on calculations using the minimum detection limit as the final concentration

8. Applicability to NSCMP

Based on the bench-scale autoclave and continuous pilot-scale testing, WAO has potential for application as a treatment for NSCMP neutralents and binary product. However, additional testing and validation of the process' performance in an extended continuous flow condition must be demonstrated. This is addressed in Section 10, Recommendations.

Based on the Pilot-scale testing, WAO has demonstrated a capability to adequately treat the H neutralent simulant feedstock. Specifically, the WAO process demonstrated at a 30:1 dilution that it could destroy the candidate compounds (including the C-S bond) in the simulant feed to levels greater than 99.99%.

Based on the test results, Zimpro has developed a full-scale processing concept to treat the candidate NSCMP wastes indicated in Table 8-1.

This is based on an estimate of the current inventory of RCWM including binary product and serves as a design benchmark for the preliminary concept design. Note that the actual design basis for the Non-Stockpile Facility has yet to be defined, and this is only a benchmark estimate used for comparison of process technologies.

Table 8-1 Candidate NSCMP Materiel to be Processed

Materiel	Total to be Processed (gallons)	Peak Generation Rate (gallons-per-day)
MEA-based H Neutralent	38,100	160
MEA-based GB Neutralent	3,000	
DF	19,640	N/A
QL	18,500	N/A

All processing operations will be conducted 5-days-per-week, 24-hours-per-day basis.

All materiel to be processed over a 24-month period.

The DF and QL will be processed in campaigns until each materiel is completed.

The MEA-based neutralent feed will vary from 0 to 160 gallons-per-day over the full 24-month period.

Based on the amounts specified in Table 8-1, and the results of the bench[13] and pilot testing, Zimpro prepared a preliminary design concept for a full-scale unit. The following sections present Zimpro's design concept including a capital cost estimate and operating requirements.

8.1 Zimpro Concept Design

The proposed processing scheme for the full-scale system is presented in Figure 8-1. The treatment scheme is divided into three stages; wet air oxidation, advanced oxidation (UV/O_3), and fluoride/ phosphorus precipitation. Note that not all of the presented unit operations may be required for each feed material. The bench autoclave and continuous pilot testing demonstrated that greater than 99% of the relevant organic contaminants are destroyed in the wet air oxidation stage. The advanced oxidation stage serves as a polishing step to remove low level residual concentrations of organic species. In addition, depending on the feed, the treated effluent may contain high concentrations of fluoride and phosphate salts. The third stage of treatment is proposed to remove fluoride and phosphate salts because these compounds may be regulated by the facility (industrial waste treatment or FOTW) that will receive the final effluent. The need for additional treatment steps and the true need for the fluoride/phosphorus precipitation stage will depend on down stream effluent requirements and amount of dilution resulting from mixing with streams from other sources.

8.1.1 Wet Air Oxidation Stage

As shown in Figure 8-1, the diluted feed is pumped to full reactor pressure before being mixed with high-pressure air from a process air compressor. The liquid feed/ air mixture is heated in the feed heater by heat exchange with high-pressure steam to a temperature sufficient to initiate the oxidation reactions. Hot oil may be used as an alternative heating medium. The hot mixture is introduced into the bottom of the reactor where the oxidation reactions initiate. The oxidized effluent exits the top of the reactor and then is cooled as they pass through an effluent cooler. The pressure of the cooled effluent is reduced to near ambient conditions before the effluent is discharged to the low-pressure separator where the non-condensable gas and liquid phases are separated. The off-gas is scrubbed as required prior to atmospheric discharge. The treated liquid from the bottom of the low-pressure separator is discharged to the advanced oxidation stage.

8.1.2 Advanced Oxidation (UV/O_3) Stage

Treated effluent from the wet oxidation system low-pressure separator will contain carbonate salts. Carbon dioxide is one of the products of oxidation in the wet air oxidation process. Due to the high pH of the process liquid, the carbon dioxide will remain in solution as a carbonate salt. Previous testing verified that the carbonate salts interfere with the UV/O_3 reactions therefore the carbonate salts must be removed prior to treatment. The WAO effluent from the low-pressure separator is fed to a mix tank where the pH is reduced by addition of acid to liberate the carbon dioxide. Once the effluent has been acidified, the stream is fed to the top of an air stripper column. Following the air stripping, the liquid stream pH is adjusted to approximately 10 to facilitate the advanced oxidation reactions. The liquid is then fed through a UV/O_3 contact cell where residual organic compounds are removed by oxidation. A commercial generator using air as an oxygen source produces ozone. The treated effluent is then fed to the fluoride/phosphate removal stage.

8.1.3 Fluoride/Phosphorus Precipitation Stage

The treated effluent from GB neutralent, DF and QL would all contain either fluoride salts or phosphate salts, or both. While the final disposition of the treated effluent has not been decided, it is likely that there will be limits imposed on the concentration of fluoride and phosphate salts that will be allowed in the final effluent. The fluoride/phosphorus precipitation stage would be included to reduce the fluoride and phosphate salts to acceptable levels prior to discharge.

Treated effluent from the advanced oxidation stage will be mixed with lime slurry in the fluoride/phosphorus precipitation stage,. The lime will react with the fluoride and phosphate to form calcium fluoride and calcium phosphate precipitate. The precipitate solids will then be removed by sedimentation in a clarifier. The clarified effluent is then discharged. The solids are collected as disposed of as appropriate.

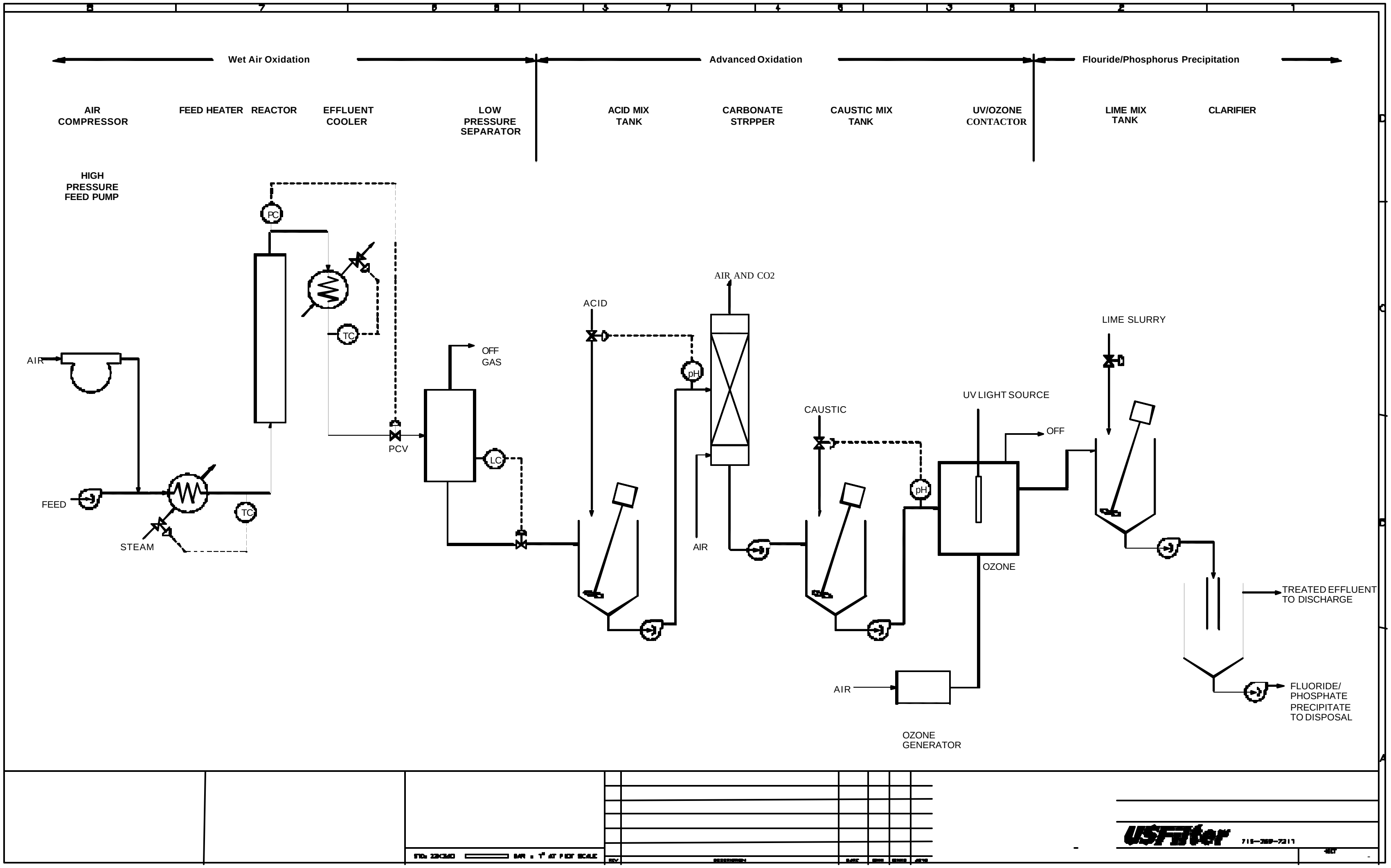

Figure 8-1 Proposed Full-scale Processing Concept

8.2 Estimated Capital and Operating Costs

Zimpro prepared an order-of-magnitude cost estimate for the processing concept described above. Note that the estimate assumes a standard industrial application, special considerations related to the installation at a government facility or handling CWM material is not included in the estimate.

8.2.1 Capital and Operating Cost - WAO

The current conceptual design for a commercial system would be a wet air oxidation system rated to process 10 gpm of diluted material at 320°C, 3200 psi with a residence time of 6 hours. The most likely material of construction would be Inconel 600 to control corrosion in the high temperature components and 316 stainless steel in the lower temperature components. The budgetary price for the wet air oxidation stage is $4,500,000. The estimated operating utilities are contained in Table 8-2 below.

Table 8-2 Full-size WAO Operating Utilities

Utility	Units	Quantity
Power	kWh/d	285
Cooling Water (30°F ΔT)	gpm	280
Fuel (Natural Gas or Fuel Oil)	Btu/h	3.7 million
Sodium Hydroxide (50 wt%)	gpm	1.2

8.2.2 Capital and Operating Cost – Post Treatment

The need for additional treatment steps including UV/O_3 oxidation and fluoride/phosphorus precipitation stage will depend on the specific installation and down stream effluent requirements.

For the purposes of this estimate, the post oxidation treatment stages including advanced oxidation and fluoride/phosphate precipitation described in the previous sections are included. The budgetary capital cost for these additional unit operations would be $1,800,000. The required utilities have not been determined.

9. Conclusions

Test data and observations were evaluated in accordance with the test criteria as described in Section 1. Test conclusions based on these criteria are summarized below.

- The Zimpro WAO process operated continuously for an 8-hour performance test at the pilot unit's maximum flow rate of 7.0 gallons-per-hour of total feed which corresponded to 0.23 gallons-per-hour of H neutralent simulant.
- Operating at a temperature of 300°C with a 60 minute residence time, the WAO process demonstrated:
    - A TOC destruction efficiency of 97.57 for H neutralent simulant producing a liquid effluent with a TOC of less than 300 ppm.
    - Carbon-sulfur bond destruction efficiencies in excess of 99.9999%.
- The WAO reactor inlet experienced blockage during work-up testing (believed due to salt precipitation) which was eliminated by instituting an hourly 5-minute water rinse. The rinse was incorporated in the performance test operating protocol and was successful. This operating philosophy should be acceptable and successful in a full-scale design.
- Post-treatment of the WAO residual using UV/Ozone oxidation could not be adequately evaluated. The WAO liquid residual contained such low levels of contaminants that the performance of the post-treatment could not be quantified.
- The liquid residuals from the process contained various concentrations of metals attributed to corrosion of the reactor vessel. Materials of construction and corrosion management need to be addressed through additional studies in subsequent phases.
- The liquid effluent from the WAO test contained trace amounts of several volatile organic compounds, but none were at a level that would pose a problem with final disposal of the liquid effluent.
- Based on the test results, Zimpro developed a preliminary full-sized processing concept. The fixed unit would process up to 10 gallons-per-minute of dilute NSCMP materiel (H and GB neutralents and DF and QL binary products). Zimpro estimated an order-of-magnitude capital cost for the WAO-only system as $ 4,500,000. Additional equipment (UV/O_3 and Fluoride/Phosphorus precipitation) may be necessary to further treat the WAO effluent before disposal, increasing the total system cost.

10. Recommendations

It is recommended that:

- The WAO full-sized processing concept should be compared to the other candidate low to moderate temperature and pressure processes (chemical oxidation and UV oxidation). If justified by the analysis, WAO testing should proceed as follows:
  - Pilot testing of all simulants should be conducted to identify the potential for plugging on the reactor system with the alternate feedstocks and evaluate operational alternatives to control or eliminate this phenomenon.
  - A material of construction and corrosion management testing program should be initiated to identify appropriate materials of construction and provide a quantitative indication of the reliability of the materials for pilot and full-scale operation. The MOC test program should include:
    - Testing of all prospective feed materiel (H and GB neutralents and DF and QL).
    - Appropriate long duration exposure of materials to WAO conditions.
    - Evaluation of achieving corrosion management through chemistry control.
    - A rigorous materials testing protocol including pre-inspection of the test coupons.
  - A series of tests should be initiated through ECBC to evaluate biotreatment of the WAO process effluent

11. References

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[11] Stone & Webster, Inc., Evaluation of the Bench-scale Testing of the Zimpro Wet Air Oxidation Process to treat NSCMP Neutralents and Binary Product Feeds, Report Number R37V-09, February, 2002.

[12] Stone & Webster, Inc., Evaluation of the Bench-scale Testing of the Zimpro Wet Air Oxidation Process to treat NSCMP Neutralents and Binary Product Feeds, Report Number R37V-09, February, 2002.

[13] Stone & Webster, Inc., Evaluation of the Bench-scale Testing of the Zimpro Wet Air Oxidation Process to treat NSCMP Neutralents and Binary Product Feeds, Report Number R37V-09 February, 2002.

Appendix A

Analytical Report Prepared By ENSR International

(Laboratory Data Sheets not Included)

A ENSR Document No. 06400-012-400

Date: December 13, 2001

Mr. Jeffrie Bettinger
Senior Lead Engineer
Stone & Webster, Inc.
100 Technology Center Drive
Stoughton, MA. 02072-4705

SUBJECT: Phase IIa Pilot-Scale Testing of the Zimpro Wet Air Oxidation Process to treat NSCMP Neutralent and Binary Product Test Report

Dear Mr. Bettinger:

ENSR International (ENSR) was retained by Stone & Webster (S&W) to conduct a sampling and analysis test program to support the Phase IIa Pilot-Scale Testing of the Zimpro Wet Air Oxidation (WAO) process to treat NSCMP Neutralent and Binary Product Feeds. A summary of the test program results and test methods employed are described below. ENSR field data sheets, calibration data and summary tables are located in appendix A. Laboratory analytical results can be found in Appendix B. Process data can be found in Appendix C.

Test Objective

The objective of the test program is to study the continuous flow operation and evaluate the reliability, process efficiency, and steady-state operation of the WAO process. In addition, the results provide engineering data to support the relationship between bench-scale test results and pilot-scale test results.

Summary of Results

ENSR International conducted the pilot-scale test program on November 15, 2001. The pilot-scale test program consisted of one 8-hour continuous performance test processing simulated H-neutralent. Two 1-hour test runs were conducted during the 8-hour performance test. Test runs were conducted during hours two and six of the process test to assess performance over time. During the 8-hour cycle the WAO process required periodic rinsing of the process stream to eliminate plugging of the system. A water rinse of the process stream was necessary and was performed for 15 minutes during the collection of sample run No. 1 to allow for continuous operation of the process.

Samples were collected through the addition of a temporary 4” ID duct following the in-line flow meter. The duct was configured to conform to EPA Method 1 to allow for a representative emission measurement. A diagram of the temporary duct can be found in Appendix A.

All samples were collected in accordance with the proposed sampling and analytical plan with the exception of the fixed gas measurements. On-site measurement of CO by the Enerac was above the 0-2000ppm range of the instrument. To acquire a CO measurement, the tedlar bag collected for VOC analysis was also analyzed for CO in the lab. Laboratory analysis determined the on-site chemical cell was encountering interference, the actual CO value was close to 0 ppm. A summary of the air emissions and fixed gas results can be found in Tables 1 and 2 respectively.

Zimpro personnel collected liquid samples with the assistance of on-site ENSR and S&W staff. Liquid effluent, simulant, and post treatment residual samples were composited over the course of each 1-hour test run. Collected samples were shipped overnight, and were maintained at 4^{o}C until analyzed. Tables 3 through 8 contain results for all liquid effluent, simulant and post treatment sample results.

Process Data

NA at this time

Sampling and Analysis

ENSR conducted two, 1-hour test runs during the eight hour test period utilizing the following parameters and methodologies. In addition, time integrated process samples were collected of the simulant, liquid effluent, and post treatment residuals.

<u>Ammonia / Moisture</u>

EPA Method CTM-027 (modified) midget sampling train was utilized for collection of Ammonia samples and were analyzed by Ion Chromatography. A sampling train containing 15mls of 0.1N sulfuric acid in the first two impingers, the third impinger remained empty and the fourth containing silica gel was utilized to collect ammonia samples. Effluent gases were drawn through a heated probe, glass fiber particulate filter and impingers at a rate of 1 liter/min for sixty minutes. At the conclusion of the test run the impingers were collected and rinsed with DI water into a glass sample jar and sent to the laboratory for analysis. In addition, the weight gain of the impingers over the course of the sampling run was utilized for determination of moisture.

<u>HCl/Cl_2</u>

An EPA Method 0050 (modified) sampling train was utilized for collection of HCl/Cl_2 samples and was analyzed by Ion Chromatography. A midget impinger sampling train containing 15mls of 0.1N sulfuric acid in the first two impingers, the third and fourth impingers contained 15mls of 0.1N NaOH and the fifth containing silica gel was utilized to collect the samples. Effluent gases were drawn through a heated probe and teflon particulate filter as well as the impingers at a rate of 1 liter/min for sixty minutes. The first two impingers were combined and impingers three and four were combined from the sampling train and were sent to the laboratory for individual analysis.

Semi-volatile Compounds

Semi-volatile organic compounds were collected in accordance with the general procedures outlined in EPA Method 18, sorbent tube procedure. The sampling train consisted of a teflon probe, an empty impinger to knock-out moisture, two XAD tubes connected in series and a personal monitoring pump calibrated at a flow rate of 500cc/min. At the completion of each sampling run, the XAD tubes were capped, labeled and shipped to the analytical laboratory for GC-MS analysis. Back to back sample tubes were analyzed separately as a check on analyte breakthrough. In addition a sample recovery study was completed in the laboratory by spiking known amounts of selected semi-volatile organics onto blank XAD tubes.

Volatile Compounds

Samples for the analysis of volatile organic compounds were collected in a tedlar bag sampling train as described in EPA Method 18. Sampling was completed by use of a “lung” type sampling system. In this procedure, a tedlar bag was connected to the source via a teflon probe and place in a sealed, rigid container. The sealed, rigid container was evacuated at a flow rate of 300cc/min, as the pressure inside the container was reduced, the tedlar bag filled at the same rate as the evacuation rate. A glass knockout impinger was placed in front of the tedlar bag to collect any condensate prior to the sample entering the bag. Condensate was collected from the impinger for run two only and was analyzed along with the tedlar bag for volatile organics. Samples were shipped to the analytical laboratory and analyzed within 72-hours of collection. Analysis of condensate was competed by purge and trap/GC-MS while analysis of the tedlar bag contents was to be completed by injecting a known quantity of sample into a GC-MS.

MEA/C-S Bonds

A sampling train containing 15mls of DI water in the first two impingers, the third impinger remained empty and the fourth containing silica gel was utilized to collect samples for determination of MEA/C-S Bonds. Effluent gases were drawn through a heated probe, glass fiber particulate filter and impingers at a rate of 1 liter/min for sixty minutes. At the conclusion of the test run the impingers were collected and rinsed with DI water into a glass sample jar and sent to the laboratory for analysis.

Total SO_x

An EPA Method 6 modified midget impinger sampling train containing 3% hydrogen peroxide in the first two impingers with the third impinger remaining empty and the fourth containing silica gel was utilized to collect SO_x samples. Effluent gases were drawn through a heated teflon probe, glass fiber particulate filter and impingers at a rate of 1 liter/min for sixty minutes. The impinger contents from the sampling train were collected and sent to the laboratory for analysis by Ion Chromatography.

O_2, CO_2, NO_x, CO – EPA Methods 3A, 7E, 10, respectively were quantified utilizing an Enerac portable multi-component chemical cell analyzer. The portable multi-component analyzer was calibrated at two points for each parameter, at the zero level and upscale calibration level utilizing EPA protocol gases. During the course of each 1-hour test run, four instantaneous readings were collected and averaged. After each test run the analyzer calibration was post-calibrated and checked for drift. In addition, a tedlar bag air sample was shipped and analyzed at the ENSR laboratory to quantify CO. CO levels in the process steam were outside the Enerac instrument range of 0-2000ppm.

Flow – ENSR utilized the installed Zimpro flow meter to calculate emission rates for each of the sampling parameters.

ENSR would like to thank Stone & Webster for the opportunity to provide these services and we look forward to working with S &W in the future. Should you have any questions concerning the contents of this report, please feel free to contact me at 978-589-3000, ext. 3504.

Sincerely yours,

Mr. James Morris
Project Manager

Attachment

TABLE 1

WAO PHASE IIA PILOT TEST AIR EMISSIONS SUMMARY

Run No.	Run 1				Run 2				Average			
Date	11/15/2001				11/15/2001							
Flow (scfm)	2.15				2.58							
Parameter		mg/M3		lb/hr		mg/M3		lb/hr		mg/M3		lb/hr
<u>Total VOCs (a)</u>												
dichloromethane		1.77		1.42200E-05		0.353161398		3.41280E-06		**1.1**		**8.8E-06**
1,2,4-trichlorobenzene		0.98		7.90174E-06		0.603826955		5.83513E-06		**0.79**		**6.9E-06**
Total SVOCs (b)		ND		ND		ND		ND		**ND**		**ND**
Hydrogen Chloride	<	1.25	<	1.0E-05	<	1.25	<	1.2E-05	**<**	**1.25**	**<**	**1.1E-05**
Chlorine	<	0.50	<	4.0E-06	<	0.50	<	4.8E-06	**<**	**0.50**	**<**	**4.4E-06**
Ammonia		8,213		6.6E-02		11,480		1.1E-01		**9,846**		**8.9E-02**
Sulfur Oxides (total)	<	1.61	<	1.3E-05	<	1.62	<	1.6E-05	**<**	**1.62**	**<**	**1.4E-05**

a. VOCs - only those VOCs present above the analytical detection limit are reported. See the analytical report in Appendix B for a list of target VOCs and detection limits.
b. SVOCs - no SVOCs were present above the analytical detection limits. See the analytical report in Appendix B for a list of target SVOCs and detection limits.

TABLE 2
WAO PHASE IIA PILOT TEST
FIXED GAS AIR EMISSIONS SUMMARY

Run No.	Run 1		Run 2		Average	
Date	11/15/2001		11/15/2001			
Flow (scfm)	2.15		2.58			
Parameter	ppm	lb/hr	ppm	lb/hr	ppm	lb/hr
A.1 NOx	1.0	1.47292E-5	2.4	4.24202E-5	**1.7**	**2.9E-05**
CO	2.0	1.9E-05	3.2	3.6E-05	**2.60**	**2.7E-05**
Parameter	%	lb/hr	%	lb/hr	%	%
A.2 CO2	0.0	N/A	0.0	N/A	**0.0**	**N/A**
O2	6.5	N/A	7.4	N/A	**7.0**	**N/A**

N/A - not analyzed

TABLE 3

PCDD/PCDF RESULTS FOR THE LIQUID EFFLUENT SAMPLES

		Method	LE	LE
Client ID:		**Blank**	**R1-PSC**	**R2-PSC**
Lab No.:		**072544 01**	**072545 01**	**072546 01**
Date Sampled:		**15-Nov-2001**	**15-Nov-2001**	**15-Nov-2001**
Component	**Units**			
Total Tetrachlorodibenzofurans	pg/L	<1.1	<1.2	<0.82
Total Pentachlorodibenzofurans	"	<0.98	<0.98	<1.1
Total Hexachlorodibenzofurans	"	<1.1	<0.99	<0.86
Total Heptachlorodibenzofurans	"	<1.4	<1.2	<1.3
Octachlorodibenzofuran	"	5.4	8.6	5.4
Total Tetrachlorodibenzo-p-dioxins	"	<1.1	1.8	<3.5
Total Pentachlorodibenzo-p-dioxins	"	<1.5	<1.8	<1.6
Total Hexachlorodibenzo-p-dioxins	"	2.2	<1.9	<2.6
Total Heptachlorodibenzo-p-dioxins	"	<2.7	<1.4	<1.3
Octachlorodibenzo-p-dioxin	"	<3.1	11	1.6
2,3,7,8-Cl4-Dibenzofuran (DB5)	pg/L	<1.1	<1.2	<0.82
2,3,7,8-Cl4-Dibenzo-p-dioxin	"	<1.1	<1.4	<1.0
1,2,3,7,8-Cl5-Dibenzofuran	"	<0.95	<0.94	<1.1
2,3,4,7,8-Cl5-Dibenzofuran	"	<1.0	<1.0	<1.2
1,2,3,7,8-Cl5-Dibenzo-p-dioxin	"	<1.5	<1.8	<1.0
1,2,3,4,7,8-Cl6-Dibenzofuran	"	<0.95	<0.84	<0.73
1,2,3,6,7,8-Cl6-Dibenzofuran	"	<0.99	<0.87	<0.76
2,3,4,6,7,8-Cl6-Dibenzofuran	"	<1.2	<1.1	<0.96
1,2,3,7,8,9-Cl6-Dibenzofuran	"	<1.4	<1.3	<1.1
1,2,3,4,7,8-Cl6-Dibenzo-p-dioxin	"	<1.7	<1.1	<1.1
1,2,3,6,7,8-Cl6-Dibenzo-p-dioxin	"	2.2	<1.0	<1.0
1,2,3,7,8,9-Cl6-Dibenzo-p-dioxin	"	<1.5	<0.98	<1.00
1,2,3,4,6,7,8-Cl7-Dibenzofuran	"	<1.2	<1.3	<1.1
1,2,3,4,7,8,9-Cl7-Dibenzofuran	"	<1.7	<1.5	<1.6
1,2,3,4,6,7,8-Cl7-Dibenzo-p-dioxin	"	<2.7	<1.4	<1.3
1,2,3,4,6,7,8,9-Cl8-Dibenzofuran	"	5.4	8.6	5.4
1,2,3,4,6,7,8,9-Cl8-Dibenzo-p-dioxin	"	<3.1	11	1.6

A.3 TABLE 4

SVOC RESULTS FOR THE LIQUID EFFLUENT SAMPLES

			Method	LE	LE
Client ID:			Blank	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**			
Phenol	1.1	ug/L	<	<	<
Bis(2-chloroethyl)ether	1.8	"	<	<	<
2-Chlorophenol	2.7	"	<	<	<
1,3-Dichlorobenzene	2.0	"	<	<	<
1,4-Dichlorobenzene	2.0	"	<	<	<
1,2-Dichlorobenzene	2.0	"	<	<	<
Bis(2-chloroisopropyl)ether	1.5	"	<	<	<
N-Nitroso-di-N-Propylamine	2.1	"	<	<	<
Hexachloroethane	2.0	"	<	<	<
Nitrobenzene	2.0	"	<	<	<
Isophorone	4.0	"	<	<	<
2-Nitrophenol	1.4	"	<	<	<
2,4-Dimethylphenol	3.5	"	<	<	<
Bis(2-chloroethoxy)methane	1.3	"	<	<	<
2,4-Dichlorophenol	1.2	"	<	<	<
1,2,4-Trichlorobenzene	2.0	"	<	<	<
Naphthalene	0.3	"	<	<	<
Hexachlorobutadiene	2.0	"	<	<	<
4-Chloro-3-Methylphenol	1.4	"	<	<	<
Hexachlorocyclopentadiene	2.0	"	<	<	<
2,4,6-Trichlorophenol	1.2	"	<	<	<
2-Chloronaphthalene	0.9	"	<	<	<
Dimethyl phthalate	1.1	"	<	<	<

Table 4 (cont)

			Method	LE	LE
Client ID:			Blank	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**			
Acenaphthylene	0.4	"	<	<	<
2,6-Dinitrotoluene	0.6	"	<	<	<
Acenaphthene	0.7	"	<	<	<
2,4-Dinitrophenol	4.8	"	<	<	<
4-Nitrophenol	1.4	"	<	<	<
2,4-Dinitrotoluene	0.5	"	<	<	<
Diethyl phthalate	1.1	"	<	<	<
4-Chlorophenylphenylether	0.9	"	<	<	<
Fluorene	0.3	"	<	<	<
4,6-Dinitro-2-methylphenol	1.5	"	<	<	<
N-Nitrosodiphenylamine	1.9	"	<	<	<
4-Bromophenylphenylether	0.3	"	<	<	<
Hexachlorobenzene	2.0	"	<	<	<
Pentachlorophenol	1.1	"	<	<	<
Phenanthrene	0.3	"	<	<	<
Anthracene	0.2	"	<	<	<
Di-n-butyl phthalate	1.1	"	<	<	<
Fluoranthene	0.2	"	<	<	<
Pyrene	0.3	"	<	<	<
Benzyl butyl phthalate	0.6	"	<	<	1.0
3,3-Dichlorobenzidine	1.0	"	<	<	<
Benzo(a)anthracene	0.2	"	<	<	<
Chrysene	0.3	"	<	<	<
Bis(2-ethylhexyl)phthalate	1.4	"	<	<	1.7
Di-n-octyl phthalate	1.1	"	<	<	<
Benzo(b)fluoranthene	0.4	"	<	<	<
Benzo(k)fluoranthene	0.4	"	<	<	<
Benzo(a)pyrene	0.5	"	<	<	<
Indeno(1,2,3-cd)pyrene	0.6	"	<	<	<
Dibenzo(a,h)anthracene	0.4	"	<	<	<

Table 4 (cont)

			Method	LE	LE
Client ID:			Blank	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**			
Benzo(ghi)perylene	0.4	"	<	<	<
N-Nitrosodimethylamine	10	"	<	<	<
Aniline	5.0	"	<	<	<
Carbazole	5.0	"	<	<	<
Benzyl alcohol	2.0	"	<	<	<
2-Methylphenol	3.2	"	<	<	<
3&4-Methylphenol	3.2	"	<	<	<
Benzoic acid	5.0	"	<	<	<
4-Chloroaniline	5.0	"	<	<	<
2-Methylnaphthalene	1.0	"	<	<	<
2,4,5-Trichlorophenol	0.8	"	<	<	<
2-Nitroaniline	5.0	"	<	<	<
3-Nitroaniline	5.0	"	<	<	<
Dibenzofuran	5.0	"	<	<	<
Benzidine	10	"	<	<	<
4-Nitroaniline	5.0	"	<	<	<

TABLE 5
INORGANIC RESULTS FOR THE LIQUID EFFLUENT, SIMULANT AND POST TREATMENT RESIDUAL SAMPLES

			Method	LE	LE	LE	SIM	SIM	SIM	SIM	PTR
Client ID:			Blank	R1-PSC	R2-PSC	R2-PSC	R1-PSC	R1-PSC	R2-PSC	R2-PSC	GRAB-PSC
Lab No.:			072544 01	072545 01	072546 01	072546 01	072547 01	072547 01	072548 01	072548 01	072694 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
A.3.1 Component	**MDL**	**Units**				Duplicate		Duplicate		Duplicate	
Alkalinity (as CaCO3)	1.0	mg/L	<	82000	79000	-	-	-	-	-	2000
pH (20 DEG C)			-	10.72	10.60	-	13.46	-	13.51	-	8.81
pH of VOC vials			7.00	11.00	11.00	-	-	-	-	-	4.00
Conductivity	4.2	uS/cm	<	50000	50000	51000	-	-	-	-	74000
TDS (180 °C)	11	mg/L	<	84000	83000	-	-	-	-	-	78000
TSS	2.0	"	<	60	67	-	-	-	-	-	66
COD	10.0	mg/L	<	1300	1800	-	-	-	-	-	8500
Ammonia (as N)	0.02	mg/L	<	3300	3300	-	-	-	-	-	2100
							(1)	-	(1)	-	
Chloride	0.05	mg/L	<	320	340	-	<0.50	-	<0.50	-	1100
Nitrate (as N)	0.050	"	<	73	79	-	<0.50	-	<0.50	-	-
Nitrite (as N)	0.05	"	-	540	600	-	-	-	-	-	5.6
Nitrite (as N)	0.010	"	<	-	-	-	<	-	<	-	0.21
Sulphate (as SO4)	0.10	"	<	450	480	-	38	-	17	-	250
Sulfite	10	mg/l	<	ND	ND	-	ND	ND	ND	-	ND
Total Organic Carbon	0.5	mg/l	<	295	276	-	9500	-	9350	9270	100

(1) Raised MDL due to dilution due to interference

TABLE 6
METALS RESULTS FOR THE
LIQUID EFFLUENT SAMPLES

			Method	LE	LE	PTR
Client ID:			Blank	R1-PSC	R2-PSC	GRAB-PSC
Lab No.:			072544 01	072545 01	072546 01	072694 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**				
				(2)	(2)	(2)
Mercury	0.05	ug/L	<	<5.0	<5.0	<5.0
			(1)			(3)
Aluminum	0.030	mg/L	<	1.3	1.3	1.1
Barium	0.001	"	<	0.033	0.016	0.031
Beryllium	0.001	"	<	<0.010	<0.010	<0.005
Cadmium	0.002	"	<	<0.020	<0.020	<0.010
Calcium	0.20	"	0.20	6.6	6.8	6.3
Chromium	0.004	"	<	11	15	9.7
Cobalt	0.010	"	<	<0.10	<0.10	<0.050
Copper	0.005	"	<	0.22	0.23	0.18
Iron	0.010	"	<	4.3	4.6	3.6
Lead	0.020	"	<	0.41	0.29	0.38
Magnesium	0.050	"	<	2.4	2.2	2.2
Manganese	0.006	"	<	<0.060	<0.060	<0.030
Molybdenum	0.010	"	<	0.13	0.21	0.13
Nickel	0.010	"	<	2.0	2.2	1.8
Phosphorus	0.060	"	<	<0.60	<0.60	0.80
Potassium	1.000	"	<	47	41	47
Silver	0.005	"	<	<0.050	<0.050	0.030
Sodium	0.100	"	0.25	31000	31000	32000
Thallium	0.060	"	<	<0.60	<0.60	<0.30
Vanadium	0.005	"	<	0.060	0.050	<0.025
Zinc	0.005	"	<	0.20	0.13	0.17

(1) Sodium laboratory contamination suspected
(2) MDL was raised due to sample dilution.
(3) 5X dilution due to matrix interference

TABLE 7
VOLATILE ORGANIC
RESULTS FOR THE LIQUID
EFFLUENT SAMPLES

			Method	LE	LE	PTR
Client ID:			Blank	R1-PSC	R2-PSC	GRAB-PSC
Lab No.:			072544 01	072545 01	072546 01	072694 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**				
				(1)	(1)	
Acetone	12.7	ug/L	<	<250	<250	160
Acrolein	5.1	"	<	<100	<100	<
Acrylonitrile	2.7	"	<	<54	<54	<
Benzene	0.5	"	<	<10	<10	<
Bromoform	0.7	"	<	<14	<14	<
Bromomethane	1.0	"	<	<20	<20	8.7
2-Butanone	3.2	"	<	<64	<64	55
Carbon Disulfide	0.9	"	<	<18	<18	<
Carbon Tetrachloride	0.7	"	<	<14	<14	<
Chlorobenzene	0.6	"	<	<12	<12	<
Chlorodibromomethane	0.4	"	<	<8.0	<8.0	<
Chloroethane	0.9	"	<	<18	<18	<
2-Chloroethylvinylether	2.8	"	<	<56	<56	<
Chloroform	0.4	"	<	<8.0	<8.0	<
Chloromethane	1.4	"	<	<28	<28	1.9
1,2-Dichlorobenzene	0.8	"	<	<16	<16	<
1,3-Dichlorobenzene	1.8	"	<	<36	<36	<
1,4-Dichlorobenzene	1.6	"	<	<32	<32	<
Dichlorobromomethane	0.4	"	<	<8.0	<8.0	<
1,1-Dichloroethane	0.5	"	<	<10	<10	<
1,2-Dichloroethane	0.4	"	<	<8.0	<8.0	<
1,1-Dichloroethene	0.7	"	<	<14	<14	<
Methyl-t-butylether	0.5	"	<	<10	<10	<

Table 7 (cont)

			Method	LE	LE	PTR
Client ID:		Blank	R1-PSC	R2-PSC	GRAB-PSC	
Lab No.:		072544 01	072545 01	072546 01	072694 01	
Date Sampled:		15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	
Component	**MDL**	**Units**				
Ethylene Dibromide	0.4	"	<	<8.0	<8.0	<
1,2-Dibromo-3-Chloropropane	10	"	<	<200	<200	<
cis-1,2-Dichloroethene	0.6	"	<	<12	<12	<
trans-1,2-Dichloroethene	0.5	"	<	<10	<10	<
1,2-Dichloropropane	0.7	"	<	<14	<14	<
cis-1,3-Dichloropropene	0.3	"	<	<6.0	<6.0	<
trans-1,3-Dichloropropene	0.6	"	<	<12	<12	<
Ethylbenzene	0.5	"	<	<10	<10	<
2-Hexanone	1.3	"	<	<26	<26	10
Methylene Chloride	2.3	"	2.4	<46	<46	<
4-Methyl-2-Pentanone	1.5	"	<	<30	<30	<
Styrene	0.6	"	<	<12	<12	<
1,1,1,2-Tetrachloroethane	0.6	"	<	<12	<12	<
1,1,2,2-Tetrachloroethane	0.8	"	<	<16	<16	<
Tetrachloroethene	0.5	"	<	<10	<10	<
Toluene	1.0	"	<	<20	<20	<
1,1,1-Trichloroethane	0.8	"	<	<16	<16	<
1,1,2-Trichloroethane	0.6	"	<	<12	<12	<
Trichloroethene	1.0	"	<	<20	<20	<
Trichlorofluoromethane	1.8	"	<	<36	<36	<
Vinyl Acetate	2.4	"	<	<48	<48	<
Vinyl Chloride	0.9	"	<	<18	<18	<
m&p-Xylene	1.1	"	<	<22	<22	<
o-Xylene	0.5	"	<	<10	<10	<

(1) Diluted due to high alkalinity
< Less than MDL

TABLE 8
ORGANIC RESULTS FOR THE LIQUID EFFLUENT AND SIMULANT SAMPLES

				LE	LE	SIM	SIM
Client ID:			MB R456	R1-PSC	R2-PSC	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01	072547 01	072548 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**					
Phenol	1.1	ug/L	<	<	<	-	-
Bis(2-chloroethyl)ether	1.8	"	<	<	<	-	-
2-Chlorophenol	2.7	"	<	<	<	-	-
1,3-Dichlorobenzene	2.0	"	<	<	<	-	-
1,4-Dichlorobenzene	2.0	"	<	<	<	-	-
1,2-Dichlorobenzene	2.0	"	<	<	<	-	-
Bis(2-chloroisopropyl)ether	1.5	"	<	<	<	-	-
N-Nitroso-di-N-Propylamine	2.1	"	<	<	<	-	-
Hexachloroethane	2.0	"	<	<	<	-	-
Nitrobenzene	2.0	"	<	<	<	-	-
Isophorone	4.0	"	<	<	<	-	-
2-Nitrophenol	1.4	"	<	<	<	-	-
2,4-Dimethylphenol	3.5	"	<	<	<	-	-
Bis(2-chloroethoxy)methane	1.3	"	<	<	<	-	-
2,4-Dichlorophenol	1.2	"	<	<	<	-	-
1,2,4-Trichlorobenzene	2.0	"	<	<	<	-	-
Naphthalene	0.3	"	<	<	<	-	-
Hexachlorobutadiene	2.0	"	<	<	<	-	-
4-Chloro-3-Methylphenol	1.4	"	<	<	<	-	-
Hexachlorocyclopentadiene	2.0	"	<	<	<	-	-
2,4,6-Trichlorophenol	1.2	"	<	<	<	-	-
2-Chloronaphthalene	0.9	"	<	<	<	-	-
Dimethyl phthalate	1.1	"	<	<	<	-	-
Acenaphthylene	0.4	"	<	<	<	-	-
2,6-Dinitrotoluene	0.6	"	<	<	<	-	-
Acenaphthene	0.7	"	<	<	<	-	-

Table 8 (cont)

				LE	LE	SIM	SIM
Client ID:			MB R456	R1-PSC	R2-PSC	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01	072547 01	072548 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**					
2,4-Dinitrophenol	4.8	"	<	<	<	-	-
4-Nitrophenol	1.4	"	<	<	<	-	-
2,4-Dinitrotoluene	0.5	"	<	<	<	-	-
Diethyl phthalate	1.1	"	<	<	<	-	-
4-Chlorophenylphenylether	0.9	"	<	<	<	-	-
Fluorene	0.3	"	<	<	<	-	-
4,6-Dinitro-2-methylphenol	1.5	"	<	<	<	-	-
N-Nitrosodiphenylamine	1.9	"	<	<	<	-	-
4-Bromophenylphenylether	0.3	"	<	<	<	-	-
Hexachlorobenzene	2.0	"	<	<	<	-	-
Pentachlorophenol	1.1	"	<	<	<	-	-
Phenanthrene	0.3	"	<	<	<	-	-
Anthracene	0.2	"	<	<	<	-	-
Di-n-butyl phthalate	1.1	"	<	<	<	-	-
Fluoranthene	0.2	"	<	<	<	-	-
Pyrene	0.3	"	<	<	<	-	-
Benzyl butyl phthalate	0.6	"	<	<	1.0	-	-
3,3-Dichlorobenzidine	1.0	"	<	<	<	-	-
Benzo(a)anthracene	0.2	"	<	<	<	-	-
Chrysene	0.3	"	<	<	<	-	-
Bis(2-ethylhexyl)phthalate	1.4	"	<	<	1.7	-	-
Di-n-octyl phthalate	1.1	"	<	<	<	-	-
Benzo(b)fluoranthene	0.4	"	<	<	<	-	-
Benzo(k)fluoranthene	0.4	"	<	<	<	-	-
Benzo(a)pyrene	0.5	"	<	<	<	-	-
Indeno(1,2,3-cd)pyrene	0.6	"	<	<	<	-	-
Dibenzo(a,h)anthracene	0.4	"	<	<	<	-	-
Benzo(ghi)perylene	0.4	"	<	<	<	-	-
Surrogate Recoveries		%					
2-Fluorophenol			62	3.0	12	-	-
d5-Phenol			44	21	42	-	-

Table 8 (cont)

				LE	LE	SIM	SIM
Client ID:			MB R456	R1-PSC	R2-PSC	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01	072547 01	072548 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**					
d5-Nitrobenzene			87	80	75	-	-
2-Fluorobiphenyl			78	73	68	-	-
2,4,6-Tribromophenol			81	5.0	24	-	-
d-14-p-Terphenyl			91	88	87	-	-
N-Nitrosodimethylamine	10	ug/L	<	<	<	-	-
Aniline	5.0	"	<	<	<	-	-
Carbazole	5.0	"	<	<	<	-	-
Benzyl alcohol	2.0	"	<	<	<	-	-
2-Methylphenol	3.2	"	<	<	<	-	-
3&4-Methylphenol	3.2	"	<	<	<	-	-
Benzoic acid	5.0	"	<	<	<	-	-
4-Chloroaniline	5.0	"	<	<	<	-	-
2-Methylnaphthalene	1.0	"	<	<	<	-	-
2,4,5-Trichlorophenol	0.8	"	<	<	<	-	-
2-Nitroaniline	5.0	"	<	<	<	-	-
3-Nitroaniline	5.0	"	<	<	<	-	-
Dibenzofuran	5.0	"	<	<	<	-	-
Benzidine	10	"	<	<	<	-	-
4-Nitroaniline	5.0	"	<	<	<	-	-
Total Tetrachlorodibenzofurans		pg/L	<1.1	<1.2	<0.82	-	-
Total Pentachlorodibenzofurans		"	<0.98	<0.98	<1.1	-	-
Total Hexachlorodibenzofurans		"	<1.1	<0.99	<0.86	-	-
Total Heptachlorodibenzofurans		"	<1.4	<1.2	<1.3	-	-
Octachlorodibenzofuran		"	5.4	8.6	5.4	-	-
Total Tetrachlorodibenzo-p-dioxins		"	<1.1	1.8	<3.5	-	-
Total Pentachlorodibenzo-p-dioxins		"	<1.5	<1.8	<1.6	-	-
Total Hexachlorodibenzo-p-dioxins		"	2.2	<1.9	<2.6	-	-
Total Heptachlorodibenzo-p-dioxins		"	<2.7	<1.4	<1.3	-	-
Octachlorodibenzo-p-dioxin		"	<3.1	11	1.6	-	-

Table 8 (cont)

				LE	LE	SIM	SIM
Client ID:			MB R456	R1-PSC	R2-PSC	R1-PSC	R2-PSC
Lab No.:			072544 01	072545 01	072546 01	072547 01	072548 01
Date Sampled:			15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001	15-Nov-2001
Component	**MDL**	**Units**					
Internal Recoveries		%					
2,3,7,8-T4CDF-13C12			72	82	74	-	-
2,3,7,8-T4CDD-13C12			61	74	64	-	-
1,2,3,7,8-P5CDF-13C12			67	75	69	-	-
1,2,3,7,8-P5CDD-13C12			70	79	83	-	-
1,2,3,4,7,8-H6CDF-13C12			95	97	86	-	-
1,2,3,6,7,8-H6CDD-13C12			89	94	89	-	-
1,2,3,4,6,7,8-H7CDF-13C12			88	83	74	-	-
1,2,3,4,6,7,8-H7CDD-13C12			90	86	89	-	-
OCDD-13C12			91	85	78	-	-
2,3,7,8-Cl4-Dibenzofuran (DB5)		pg/L	<1.1	<1.2	<0.82	-	-
2,3,7,8-Cl4-Dibenzo-p-dioxin		"	<1.1	<1.4	<1.0	-	-
1,2,3,7,8-Cl5-Dibenzofuran		"	<0.95	<0.94	<1.1	-	-
2,3,4,7,8-Cl5-Dibenzofuran		"	<1.0	<1.0	<1.2	-	-
1,2,3,7,8-Cl5-Dibenzo-p-dioxin		"	<1.5	<1.8	<1.0	-	-
1,2,3,4,7,8-Cl6-Dibenzofuran		"	<0.95	<0.84	<0.73	-	-
1,2,3,6,7,8-Cl6-Dibenzofuran		"	<0.99	<0.87	<0.76	-	-
2,3,4,6,7,8-Cl6-Dibenzofuran		"	<1.2	<1.1	<0.96	-	-
1,2,3,7,8,9-Cl6-Dibenzofuran		"	<1.4	<1.3	<1.1	-	-
1,2,3,4,7,8-Cl6-Dibenzo-p-dioxin		"	<1.7	<1.1	<1.1	-	-
1,2,3,6,7,8-Cl6-Dibenzo-p-dioxin		"	2.2	<1.0	<1.0	-	-
1,2,3,7,8,9-Cl6-Dibenzo-p-dioxin		"	<1.5	<0.98	<1.00	-	-
1,2,3,4,6,7,8-Cl7-Dibenzofuran		"	<1.2	<1.3	<1.1	-	-
1,2,3,4,7,8,9-Cl7-Dibenzofuran		"	<1.7	<1.5	<1.6	-	-
1,2,3,4,6,7,8-Cl7-Dibenzo-p-dioxin		"	<2.7	<1.4	<1.3	-	-
1,2,3,4,6,7,8,9-Cl8-Dibenzofuran		"	5.4	8.6	5.4	-	-
1,2,3,4,6,7,8,9-Cl8-Dibenzo-p-dioxin		"	<3.1	11	1.6	-	-
Dilution Factor			1.0	1.0	1.0	-	-

Appendix B

Analytical Data Prepared
by
Southwest Research Institute
(Laboratory Data Sheets not Included)

B SwRi Data
Work Order 21315

System ID (SwRI)	171256	171257
Sample ID	MEA/CS Bonds-R1-IMP123	MEA/CS Bonds-R2-IMP123
Analytes		
MEA (ug/mL)	1.0 U	2
Bonds (C-S) (%)	0.5 U	0.5 U
DMSO (ug/mL)	<0.10 U	
Whenever a blank space appears for an analyte, the COC did not require an analysis for that compound. Analyses noted with a "U" were not detected, the result shown is the MDL		

Work Order 21316

System ID (SwRI)	171259	171260	171261	171262	171263	171264	171265	171266	171267
Sample ID	LE-R1-SW	LE-R1-VOA-SW	LE-R2-SW	LE-R2-VOA-SW	MEA/CS BONDS-DIH2O BLK	SIM-R1-SW	SIM-R1-VOA-SW	SIM-R2-SW	SIM-R2-VOA-SW
Analytes									
Hexafluorobenzene (ug/L)		1.0 U		1.0 U			1.0 U		1.0 U
Dichloroethane (DCE) (ug/L)		1.0 U		1.0 U			270		290
Chloromethane (ug/L)		580		270			1.1		1.2
Vinyl chloride (ug/L)		1.3		2.1			33		45
Bromomethane (ug/L)		62		15					
Chloroethane (ug/L)							1.2		1.1
Acetone (ug/L)		36		46			32		27
Carbon disulfide (ug/L)		1.5		1.4			1.6		4.2
Butanone (ug/L)							5.2		5.8
Bromoform (ug/L)							1.3		1.5
Acetaldehyde (ug/L)							60		100
Propanol (ug/L)				9			5		
Trimethyl silanol							10		
Fluorotrimethylsilane (ug/L)									8
Diisoocty Diphosphoric acid (ug/L)									9
2-hydroxy-propanamide (ug/L)		50							
Carbon oxide sulfide (COS) (ug/L)				1000					
Methoxy acetic acid (ug/L)				9					
Methyl ester thiocyanic acid (ug/L)				9					
Ethyl ester thiocyanic acid (ug/L)		20		9					
Methyl ethyl disulphide (ug/L)				2					
Diethyl disulfide (ug/L)		200		40					
2-Propanamine (ug/L)		50							
MEA (ug/mL)	2		1.0 U		1.0 U	34,000		40,000	
Dimethylsulfoxide (DMSO) (ug/mL)		0.10		<0.10 U			545		530
Bonds (C-S) (%)	0.5 U		0.5 U		0.5 U	DMSO		DMSO	
Methylsulfonic acid (MSA) (ug/L)	10 U		10 U						

Whenever a blank space appears for an analyte, the COC did not require an analysis for that compound.
Analyses noted with a “U” were not detected, the result shown is the MDL

Work Order 21321

System ID (SwRI)	171310	171311
Sample ID	PTR-GRAB-SW	PTR-GRAB-VOA-SW
Analytes		
Hexafluorobenzene (ug/L)		1.0 U
Dichloroethane (DCE) (ug/L)		0.91
Chloromethane (ug/L)		4.5
Vinyl chloride (ug/L)		0.55
Bromomethane (ug/L)		0.53
Chloroethane (ug/L)		0.58
Acetone (ug/L)		420
Methylene chloride (ug/L)		15
Carbon disulfide (ug/L)		2.6
Butanone (ug/L)		96
Hexanone (ug/L)		18
Acetaldehyde (ug/L)		300
Fluorotrimethylsilane (ug/L)		2
Propanenitrile (ug/L)		3
Butanal (ug/L)		30
Acetic acid (ug/L)		4
Heptanone (ug/L)		100
MEA (ug/mL)	1.0 U	
Dimethylsulfoxide (DMSO) (ug/mL)		<0.10 U
Bonds (C-S) (%)	0.5 U	
Methylsulfonic acid (MSA) (ug/L)	50 U	
bis(2-Ethylhexyl)phthalate (ug/L)	37	
Whenever a blank space appears for an analyte, the COC did not require an analysis for that compound. Analyses noted with a "U" were not detected, the result shown is the MDL		

Appendix C

Selected Procedures Prepared
by
U.S. Filter/Zimpro

C Pilot Scale WAO Operational Procedures

The following procedure was used to make the desired feedstock.

1. Approximately 75 percent of the required water was put into the mix tank.

2. The tank mixer was turned on.

3. The required quantity of monoethanolamine was added.

4. The cooling water flow was started to the heat exchanger.

5. The recycle pump was started and the mix tank contents were circulated through the heat exchanger and back to the mix tank. This was done until the temperature was below 70°F. No significant temperature increase was noted upon mixing the MEA and water.

6. The required quantity of 1-2 dichloroethane was added to the mix tank. A reaction time of 15 minutes was allowed before any additional chemicals were added.

7. The required quantity of dimethyl sulfoxide was added to the mix tank. A reaction time of 10 minutes was allowed before any additional chemicals were added.

8. The required quantity of 50% sodium hydroxide was added. This quantity was based on laboratory bench scale testing. The sodium hydroxide was required to maintain the pH of the oxidized liquor above 10.

9. The remaining quantity of softened water was added. The final quantity of water was corrected for the volume of water added with the sodium hydroxide and the desired final dilution ratio for the WAO feedstock.

10. The feedstock was then pumped to the feed tank.

The following sequence was used in starting, operating and shutting down the WAO pilot unit.

1. The desired feedstock was mixed in the stainless steel mix tank. The feedstock mixture composition is presented in Section 4.2 of this report.

2. The low pressure re-circulation feed pump was started recirculating feedstock to the feed tank, bypassing the high pressure pump.

3. The high pressure pump was started on water.

4. The air compressor was started. Air was introduced to the system slowly increasing the flow until the desired value was attained.

5. The pressure controller was adjusted to maintain the correct reactor pressure.

6. The oil heater was started. The oil mixer was started.

7. The unit was heated up on water and air.

8. As the unit was heated up, the water and process air flows were adjusted to the desired values.

9. The computer data logger was started and recording of data on the log sheets was started.

10. The ESD and Sybron oxygen analyzers were started and calibrated.

11. The gas chromatograph was started and calibrated.

12. The cooling water system for the oxidized liquor coolers was started and adjusted to the desired temperature.

13. The pilot unit effluent was collected, weighed and sampled on half hour intervals by the assistant operator. The specific gravity and pH was also recorded.

14. The computer and field log readings were recorded hourly by the lead operator.

15. When the reactor bottom temperature reached approximately 475°F and the liquid and air flow rates were well established, the high pressure pump was switched from water to the feedstock.

16. Once on feedstock, all effluent was collected and placed in barrels for disposal.

17. The air rate was adjusted to obtain the desired offgas oxygen concentration.

18. The oil preheater temperature was adjusted to obtain the desired reactor top temperature.

19. Hourly grab samples of oxidized liquor were taken for archive purposes.

20. Hourly grab samples of offgases were taken for analysis.

21. When the pilot unit was at the desired operational parameters of temperature, pressure, flowrate and offgas oxygen, the work-up tests were conducted to

determine the operational parameters and procedures to be used in the performance test on the H in MEA simulant.

22. Upon completion of the 5 work-up tests, the process operating parameters and operational procedures for the performance test were established.

23. The performance test was conducted for an 8 hour period.

24. Feedstock samples were taken at the beginning of the 2nd and 6th hours of the test period.

25. Throughout the test period, the data logging and sampling as discussed above were followed with the addition of a composite oxidized liquor sample made by accumulating grab samples taken hourly and in a composite pail. The composite sample was collected for distribution at the end of the test.

26. Additional samples of oxidized liquor were taken at the conclusion of the 2nd and 6th hours for analysis by an independent laboratory under contract with STONE & WEBSTER.

27. Using impinger sampling techniques, the offgas stream before the water scrubber was tested for ammonia, sulfur oxides and nitrogen oxides content during the 2nd and 6th hours of the performance test.

28. During the performance test, each hour at 10 minutes after the hour, the unit was switched from feedstock to water for a 5 minute period to rinse the line from the oil heater to reactor inlet. This water rinse procedure was instituted to avoid accumulation of a potential flow restriction in the line. This water rinse procedure allowed reliable operation of the WAO unit.

29. At the conclusion of the 8 hour performance test, at the request of STONE & WEBSTER, a extended demonstration performance test was conducted following the same procedures above with the exception of the water rinse.

30. The test program was finished upon completion of the extended demonstration performance test and the pilot unit was shutdown.

31. The oil heater was shutdown.

32. The pilot unit was switched from feedstock to water and the feed recirculation pump was shutdown.

33. When the reactor outlet temperature reached 200°F the system was depressurized by adjusting the pressure controller.

34. The process air compressor was shutdown.

33. The high pressure pump was shutdown.

34. The data logger was shutdown.

35. All liquors collected from the WAO study, including all remaining mixed feedstock were stored for disposal at a licensed incineration facility at a later date.

Appendix D

Workup and Performance
Test Summary Sheets

D Test Summary Sheets

D.1 Workup Tests

D.1.1 Workup Test 1

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	320°C (608°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 20

OBJECTIVES:

Operate at the above conditions to get baseline data on the treatment of the H in MEA to determine operational procedures and parameters for the performance test.

SCHEDULE:

Start of test	Monday November 12, 2001	1400 hrs
End of test	Monday November 12, 2001	2130 hrs

TIMELINE:

Monday, November 12, 2001

0600	Configure and begin heating up pilot unit on water
1200	Complete mixing feedstock
1400	Pilot unit on feedstock – 20:1 dilution Begin work-up test No. 1
1557	High reactor inlet pressure, on water
1614	High pressure cleared, on feedstock
1615–2130	Switched between feedstock & water several times due to high reactor inlet pressure
2130	Concluded work-up test No. 1

OBSERVATIONS:

A high pressure drop (in excess of 200 psig) was noted between the oil heater outlet and the reactor top. The pressure drop would clear after operation on water for several minutes. This indicates a deposit of a highly water soluble material, most likely sodium carbonate, is depositing in the reactor inlet line or at the bottom of the reactor. The pilot unit was operated for a 5 hour period with numerous water rinses conducted. Each water rinse was for a duration of several minutes. Conduct the next work-up test at the same operational parameters, but at a higher feed dilution, 25 : 1.

D.1.2 Workup Test 2

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	320°C (608°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 25

OBJECTIVES:

Repeat the operating parameters of work-up test No. 1 with a higher feedstock dilution (25 : 1 compared to 20 : 1). This will decrease the concentration of carbon dioxide (sodium carbonate) formed during the WAO reaction.

SCHEDULE:

Start of test	Monday November 12, 2001	2130 hrs
End of test	Monday November 12, 2001	2400 hrs

TIMELINE:

Monday, November 12, 2001

2130	Begin work-up test No.2 with feedstock at 25: 1 dilution
2340	High reactor inlet pressure, on water
2350	High pressure cleared, on feedstock
2400	Concluded work-up test No. 2

OBSERVATIONS:

The high pressure drop between the oil heater outlet and the reactor top was again noted. A water rinse would remove the blockage in several minutes, the same as observed during work-up test No. 1. Conduct the next work-up test at the same operational parameters, but at a higher feed dilution, 30 : 1.

D.1.3 Workup Test 3

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	320°C (608°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 30

OBJECTIVES:

Repeat the operating parameters of Work-up test No. 2 with a higher feedstock dilution (30 : 1 compared to 25 : 1). This will further decrease the concentration of carbon dioxide (sodium carbonate) formed during the WAO reaction. This may allow operation below the solubility limit of sodium carbonate at the reactor operating conditions.

SCHEDULE:

Start of test	Tuesday November 13, 2001	0000 hrs
End of test	Tuesday November 13, 2001	0320 hrs

TIMELINE:

Tuesday, November 13, 2001

0000	Begin work-up test No.3 with feedstock at 30:1 dilution
0015	Pressure control valve gasket failed Switched to stand-by valve, set pressure not maintained Bottled reactor to fix pressure control valves
0130	Pilot unit heating up on water
0240	Pilot unit on feedstock
0320	Reactor top gasket filler material failed Pilot unit shutdown Higher temperature gaskets ordered Concluded work-up test No. 3

OBSERVATIONS:

Testing was never completed at the test conditions due to a mechanical failure of the PCV gasket. The gasket material was replaced in both PCVs and operation was continued. After 40 minutes of operation, the reactor top gasket failed and the pilot unit was cooled down for replacement of the reactor gaskets. It was determined that the filler material in the reactor gaskets was not able to operate at the reactor temperature desired. Higher temperature gaskets were ordered and installed upon arrival. Operate at the test parameters of Work-up test No. 3.

D.1.4 Workup Test 4

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	320°C (608°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 30

OBJECTIVES:

Repeat operation at the testing parameters of work-up test No. 3 with the higher temperature reactor gaskets installed. To better determine the location of the deposit causing the pressure drop, a pressure sensor was installed in the line from the oil heater several inches ahead of the reactor.

SCHEDULE:

Start of test	Wednesday November 14, 2001	1400 hrs
End of test	Wednesday November 14, 2001	1950 hrs

TIMELINE:

Wednesday, November 14, 2001

0900	Replacement gaskets arrive and are installed in reactor
1000	Begin heating up pilot unit on water
1200	Feedstock is mixed and transferred to feed tank
1400	Pilot unit on feedstock Begin work-up test No.4 with feedstock at 30:1 dilution
1730–1950	Switched between feedstock & water several times due to high reactor inlet pressure
1950	PCV B seat failed, switched to PCV A, on water
2015	Pilot unit on feedstock
2030	PCV A would not maintain pressure Bottled reactor to replace gasket in PCV B Concluded work-up test No. 4

OBSERVATIONS:

The high pressure drop between the oil heater outlet and the reactor inlet was again noted. With the newly located pressure sensor close to the reactor bottom, it was determined that the deposits that were observed earlier most likely occurred in the line several inches ahead of the reactor, not in the very bottom of the reactor or higher up in the reactor. A water rinse would remove the blockage in several minutes. The pilot unit was operated for a 2½ hour period with numerous water rinses conducted. Each water rinse was for a several minute duration. A second failure of the PCV gasket material occurred at the conclusion of the test period. A different type of gasket material was installed. The prior material was not suitable for the current operating conditions. Conduct testing at a reactor temperature of 300°C (572°F) and a feedstock dilution of 30 : 1. During operation conduct a 5 minute water rinse each hour.

D.1.5 Workup Test 5

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	300°C (572°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 30
g.	Water Rinse	5 minutes every hour

OBJECTIVES:

Determine the operability of the WAO system at a reactor temperature of 300°C (572°F) and a feedstock dilution of 30 : 1. A 5 minute water rinse will be conducted each hour to maintain a minimal pressure increase at the reactor inlet.

Prior to beginning the test, the pilot unit will be rinsed with water for two hours at temperature to remove any residual solids build-up from the previous testing.

SCHEDULE:

Start of test	Wednesday November 14, 2001	2315 hrs
End of test	Thursday November 15, 2001	0800 hrs

TIMELINE:

Wednesday, November 14, 2001

2115	Pilot unit on water for rinse
2315	Pilot unit on feedstock Begin work-up test No. 5

Tursday, November 15, 2001

0015	Pilot unit on water for 5 minute rinse
0020	Pilot unit on feedstock
0115	Pilot unit on water for 5 minute rinse
0120	Pilot unit on feedstock
0215	Pilot unit on water for 5 minute rinse
0220	Pilot unit on feedstock
0300	Continue work-up test No. 5, with a 5 minute water rinse 15 minutes after each hour
0315	Conduct 5 minute water rinse
0410	Conduct 5 minute water rinse
0510	Conduct 5 minute water rinse

0610	Conduct 5 minute water rinse
0710	Conduct 5 minute water rinse
0800	Conclude work-up test No. 5

OBSERVATIONS:

The pilot unit operated smoothly for 8 3/4 hours with minimal pressure increase at the reactor inlet. The pressure spikes were noted between the reactor inlet pressure sensor. Conduct the performance test at the operational parameters and the procedures of work-up test No. 5.

D.2 Performance Test

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	300°C (572°F)
b.	Reactor outlet pressure	3200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 30
g.	Water Rinse	5 minutes every hour

OBJECTIVES:

Conduct the Performance Test at the above operational parameters with a water rinse for 5 minutes each hour.

SCHEDULE:

Start of test	Thursday November 15, 2001 0800 hrs
Begin 2nd hour sampling	Thursday November 15, 2001 0900 hrs
Conclude 2nd hour sampling	Thursday November 15, 2001 1000 hrs
Begin 6th hour sampling	Thursday November 15, 2001 1300 hrs
Conclude 6th hour sampling	Thursday November 15, 2001 1400 hrs
End of test	Thursday November 15, 2001 0800 hrs

TIMELINE:

Thursday, November 15, 2001

0800	Begin 8 hour performance test with 5 minute water rinse, 10 minutes after each hour
0810	Conduct 5 minute water rinse
0900	Conduct the 2nd hour sampling test
0910	Conduct 5 minute water rinse
0940	Air flow dropped apparently due to foreign particle in the air flow control needle valve. Flow restored by fully opening the needle valve momentarily then returning it to its original setting. Low offgas oxygen concentration was observed for a few minutes.
1000	Conclude the 2nd hour sampling test
1010	Conduct 5 minute water rinse
1110	Conduct 5 minute water rinse
1210	Conduct 5 minute water rinse

1300	Conduct the 6^{th} hour sampling test
1310	Conduct 5 minute water rinse
1320	Air flow dropped. Same as 0940 above.
1400	Conclude the 6th hour sampling test
1410	Conduct 5 minute water rinse
1510	Conduct 5 minute water rinse
1600	Conclude 8 hour performance test

OBSERVATIONS:

The pilot unit operated with minimal pressure increase at the reactor inlet during the 8 hour test period. A slight decrease in the offgas oxygen occurred due to foreign material becoming lodged in the air flow control valve. Opening and readjusting the valve cleared the material. This is due to the extremely small orifice in the control valve required for proper control.

The Performance Test validated the WAO operational parameters and procedures for the H in MEA material. The Performance Test demonstrated the WAO process efficacy in treating H in MEA simulant in a continuous flow WAO unit. The continuous flow WAO pilot unit, configured to simulate a full scale WAO system, operated for an eight hour steady period in a continuous, reliable and safe manner.

At the completion of the Performance Test, an Extended Duration Performance Test was conducted at the request of the Stone & Webster. The purpose was to determine if the pilot unit could be operated for 4 hours without a water rinse and not incur a permanent pressure build-up at the reactor inlet.

D.3 Performance Test – Extension

TARGET PROCESS PARAMETERS:

a.	Reactor outlet temperature	300°C (572°F)
b.	Reactor outlet pressure	3,200 psig
c.	Offgas residual oxygen	5 %
d.	Nominal liquid residence time	1 hour
e.	Feedstock	H in MEA
f.	Dilution Ratio	1 : 30
g.	Water Rinse	None

OBJECTIVES:

Determine if the WAO pilot unit can be operated for a four hour period at the Performance Test operational parameters without a water rinse and not incur a permanent pressure build-up at the reactor inlet.

SCHEDULE:

Start of test	Thursday November 15, 2001	1515 hrs
End of test	Thursday November 15, 2001	1915 hrs

TIMELINE:

Thursday, November 15, 2001

1510	Conduct 5 minute water rinse
1515	Begin 4 hour Extended Duration Performance Test
1915	Conclude Extended Duration Performance Test Pilot unit on water for shutdown and decommissioning.

OBSERVATIONS:

During the test period the pilot unit experienced several increased pressure drop excursions which lasted several minutes between the reactor inlet and the reactor outlet. The blockage would clear after several minutes without any water rinses.

The testing was successfully completed. The pilot unit was shutdown and decommissioned.